THE LIGHTFASTNESS OF AND SUBSTRATE PHOTOTENDERING INDUCED BY TRIAZINYLAMINO STILBENE FLUORESCENT WHITENING AGENTS ON COTTON

by

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INTRODUCTION

Fluorescent whitening agents are used in textile processing to improve the inherent optical properties of fibers, obscure the yellowness caused by impurities, impart brillance to apparel items which satisfies certain fashion requirements, and achieve certain special effects which could not otherwise be obtained (5). In addition, fluorescent whitening agents reduce the amount of chemical bleaching required to obtain desired levels of whiteness in fabrics. Because of the many inherent advantages of fluorescent whiteners, compared to chemical bleaching, they have attained widespread use in the textile industry for improving fabric whiteness (22,54).

Fluorescent whitening agents are applied to a variety of textile products, including sportswear, dressgoods, shirtings, undergarments, and sheetings which vary in fiber content and construction characteristics. Textiles that are to remain white or are to be dyed pastel shades frequently are fluorescently whitened. They also are used extensively in laundry detergent formulations, which represents approximately 40% of the total volume produced annually, to renew the whiteness of soiled or discolored items.

A fluorescent whitening agent functions by absorbing ultraviolet radiation present in sunlight or artificial light and converting it to visible blue light. By increasing the amount of blue light reflected from a fabric, the apparent whiteness is increased. Hence, the yellow hue of the fabric is decreased, the fabric becomes bluer, and the total reflectance or brightness is increased. Greater brightness is obtained when the total amount of light reflected in the visible portion of the spectrum is increased without changing the absorption spectra.

Sunlight contains a considerable amount of ultraviolet radiation, whereas artificial light sources have varying amounts, depending on the spectral distribution and intensities of the ultraviolet wavelengths present. Because of the higher energy associated with ultraviolet radiation, compared to visible electromagnetic radiation, there is a greater potential for fiber degradation when the absorption of ultraviolet radiation by textile substrates is increased (65). Hence, fluorescent whitening agents may accelerate actinic degradation in fibers due to the increase in the amount of UV radiation absorbed. Some researchers (2,17,26,30) have speculated, however, that fluorescent whitening agents absorb the harmful light, thereby screening the fiber and actually decreasing degradation, thus acting as an ultraviolet absorber.

As in the case of certain dyestuffs, many fluorescent whitening agents have poor lightfastness, and their effectiveness may be reduced appreciably upon exposure to light. The relationship between the inherent lightfastness of a fluorescent whitening agent and its potential for promoting actinic degradation in fiber substrates has not been adequately assessed. Hence, the purpose of this study was to evaluate how the chemical structure of triazinyl amino stilbene fluorescent whitening agents influence their lightfastness and potential for causing photochemical degradation in cotton.

REVIEW OF LITERATURE

Most textile fibers are not completely white, hence, efforts have been made since ancient times to improve fabric whiteness. Cotton, flax, silk, wool, and other natural fibers are not perfectly white due to the presence of certain colored impurities which increase the absorption of incident light in the blue region of the electromagnetic spectrum, resulting in a yellow tinge. Similarly, the whiteness of man-made fibers often is less than satisfactory because of the inherent light absorbing qualities of the polymeric structure, manufacturing conditions, or impurities. Polyester, for example, has a cream-colored appearance which often is modified by a variety of methods to improve its appearance. Many of the high temperature fibers such as Kevlar (yellow) and Nomex aramid (beige) have a distinct color because of the degree of unsaturation and conjugation in the polymeric chains. The distinct coloration in these fibers limits their suitability for certain applications.

Methods of Improving Fabric Whiteness

A variety of methods have been used to remove the yellowish tinge in natural and man-made fibers. The earliest method for improving the whiteness of cotton and linen fabrics was sun bleaching or grassing in which fabrics were layed out in the sun (84). Because sun bleaching was not an efficient method of improving fabric whiteness, it was replaced by chemical bleaching methods in the early 1800's. Chemical bleaching agents discolor or destroy the impurities by oxidation or reduction mechanisms. If not carefully controlled, however, oxidative bleaches can attack not only the impurities but the fibers as well (29). Reducing type bleaches such as sulfur dioxide often are used to improve the whiteness of protein fibers, however, the bleaching effect is less permanent, and impurities may be oxidized back to the original color upon exposure to air, especially in sunlight (84).

Even well bleached textiles possess a yellowish appearance. Hence, additional methods that have been employed to further improve the whiteness of chemically bleached fibers. For example, certain blue dyestuffs or pigments (blueing agents) were applied to fabrics, both commercially and in home laundering, which would increase the absorption of the yellow wavelengths of incident light, thereby imparting a blue tint to the fabric (20,84). This often is referred to as physical bleaching, tinting or blueing, to distinguish it from chemical bleaching (20,70,84,91). By introducing a color complimentary to that of the impurities, the light reflected in the yellow portion of the spectrum is reduced to the same level as the wavelengths in the blue region of the electromagnetic spectrum (70). Hence, the relative intensities of the various wavelengths of reflected light are more uniform throughout the spectral range. As a result, the surface appears whiter because yellowness is decreased, but it is much duller or greyish because there is a reduction in the total light reflected (84).

The use of blueing agents was substantially reduced by the development of fluorescent whitening agents which improve whiteness by increasing total reflectance (70). In general, fluorescent whitening agents are colorless, fluorescent organic compounds which are exhausted onto fibere much like a dyestuff. They absorb invisible, long wavelength ultraviolet radiant energy and re-emit the energy back in the form of longer wavelength, visible blue light (16,77). Thus, they not only improve the distribution of light over the spectral range, but also add to the total amount of light reflected, resulting in whites of outstanding brightness (84).

The effects of blueing and fluorescent whitening on the reflectance curves of bleached cotton are illustrated in Figure 1.

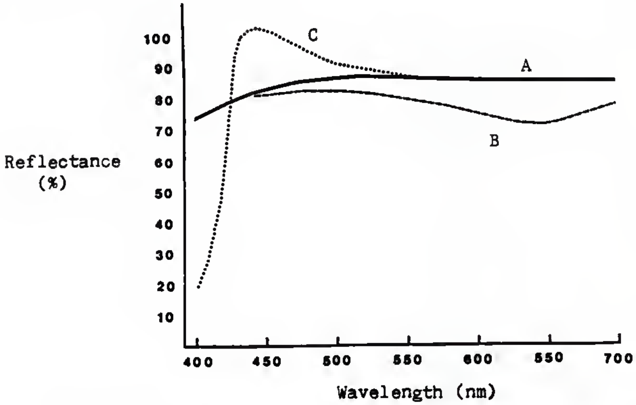


Figure 1. Reflectance Curves of Whitened Cotton. A: bleached cotton, B: addition of a blueing agent, and C: addition of a fluorescent whitening agent.

The bleached cotton (curve A) shows greater reflectance in the yellow portion of the visible spectrum than in the blue region, imparting a yellow cast. With the addition of a blueing agent (curve B), less light is reflected overall due to greater absorption in the yellow region. The shape of the curve more closely approximates an ideal white (a line parallel to the horizontal axis at 100% reflectance) than the curve of the bleached cotton. However, the fabric appears more gray because of the decrease in overall reflectance. The addition of a fluorescent whitening agent (curve C), results in a peak in the blue region. Hence, the total amount of light reflectsd is increassd without changing the rest of the spectrum, thersby producing a more perceivable white with a bluish fluorescence.

Fluorescent whitening agents are known by a variety of names, i.e., optical bleaching agents, fluorescent bleaching agents, optical brightening agents, optical brightensrs, optical whitening agents, whiteners, etc. (26,77). Colour Index refers to these compounds as fluorescent brightening agents. However, the nomenclature suggested by the American Society for Testing and Materials (ASTM) of fluorescent whitening agents or FWA´s for short, will be used in this study (77).

History of the Development of FWA´s

The theoretical basie behind fluorescence was investigated by physicist George Gabriel Stokes in 1852 (91). He demonstrated that many substances could absorb ultraviolet radiation and re-emit it as visible light without any chemical changes taking place in the molecules. The term fluorescence wae used to describe this phenomenon. In 1921 A.V. Lagorio observed that certain dyestuffs reflected more visible radiation than was initially absorbed from the incident light (91). His discovery of fluorescsnt dyes lead to the development of FWA´s.

The commerical significance of FWA´s resulted from a discovery by Paul Krais in 1929 (70,91). He found that a fully bleached appearance could be obtained from partially bleached flax by treating it with a solution of aesculin, a blue fluorescent glucoside of 6,7-dihydroxycoumarin obtained from horse-chestnut husks (16). The poor washfastness of aesculin as well as its tendency to discolor to a yellow-brown when exposed to light limited its commercial success as an FWA (26,77,91).

The first synthetic FWA (a diacyl derivative of 4,4´-diaminostilbene-2,2´-disulphonic acid) which exhibited affinity towards cellulosic textiles and paper was patented by ICI (Imperical Chemical Industries) in 1934 (91). Similarly in 1935 Hoffmanns Starkefabrik and Ultrazell GmbH patented a process for whitening cellulose using B-methylumbelliferone and 4-methyl-7-dimethyl-amino coumarin (20,77). However, these compounds were not fast to washing. The first industrial breakthrough came in 1940 when Bruno Wendt and coworkers at I.G. Farben found that triazinylaminostilbenes (derivatives of 4-4´-diaminostilbene-2,2´-disulphonic acid) exhibited substantivity on cellulosic textiles and could be exhausted from detergents and alkaline baths (20,77). The discovery of triazinylaminostilbenes, which are still commercially important today, resulted in the rapid development of FWA´s. Most of the FWA´s available at this time were only suitable for cellulosic textiles, however, they were needed to whiten other fibers as well. In 1942 FWA´s based on bis-benzimidazole were marketed for use on both cotton and polyamides, in 1945 derivatives of bis-benzoxazole were developed for use on plastics and synthetic fibers, and in 1948 derivatives of 7-amino-coumarin were developed for wool and polyamide (75). Research continued and in 1948 FWA´s based on 1,4-bis-(styryl)benzene and 4,4´-bis-(naphthotriazolyl)stilbene were produced for cotton, wool, and synthetic fibers. Other developments included derivatives of pyrazoline for polyacrylonitrile and polyamide (1949), stilbyltriazoles (1951), naphthalic acid imides (1952), 3-phenyl-7-aminocoumarin (1954), and pyrazine (1957) (91)

In the years following, FWA´s were developed from derivatives of substances already in use and from new substances. Today the majority of FWA´s are based on 4,4´-diaminostilbene-2,2´-disulphonic acid, coumarin, pyrazoline, styryloxazole, distyrylbenzene, naphthalene dicarboxylic acids, and heterocyclic acids (91).

Fluorescence

Fluorescent organic compounds are characterized by their ability to absorb ultraviolet radiation and re-emit it as visible light; whereas nonfluorescing compounds dissipate the absorbed radiation as heat (3). When fluorescent compounds absorb ultraviolet radiation, electrons in the ground state pass into a higher energy or excited state, and then return to the ground state with re-emission of light quanta slightly smaller than that absorbed. Some energy is lost and, thus, the emitted light is of a lower frequency and longer wavelength than the absorbed radiation by approximately 100 nm (91). The excited electrons return to the ground state within 10^{-8} to 10^{-9} seconds. The shorter the length of time between absorption and re-emission of the electromagnetic radiation, the less difference there is between the wavelengths of absorbed and emitted light, and the greater the fluorescence because the molecules have less time for dissipating the energy as heat (3). Fluorescent materials do not have an afterglow, as phosphorescent materials do, and only emit light as long as they are excited.

In order for a molecule to fluoresce, it must possess a large conjugated system, with the easily excited π (pi) electrons facilitating the absorption of ultraviolet radiation (19). Chemical groups that are necessary for fluorescence are called fluorophors or fluorogens and are of the type -CH=CH-, -CO-, and -CH=N- (26). They can be incorporated into straight chains, aromatic, or heterocyclic compounds (20). Very few aliphatic or saturated cyclic compounds fluoresce because they contain electrons which are tightly bound or involved in σ (sigma) bonds. When the electrons in saturated molecules absorb ultraviolet energy and are promoted to the excited state, the result is usually bond dissociation. Energy dissipated as a result of chemical bonds breaking does not result in fluorescence (77).

Many factors influence the extent to which chemical compounds fluoresce. The most intense fluorescent aromatic molecules have a rigid planar structure (36). When aliphatic double bonds are present, the compounds may exhibit trans to cis isomerism. The cis isomers are non-fluorescent, while the trans isomers show intense fluorescence (77). Substituents on a molecule also influence its potential to fluoresce. Auxochromes, for example, may contribute to water solubility, substrate affinity, and the development of the desired color but may or may not affect fluorescence. Auxochromic groups include alkyl ($-CH_3$, $-(CH_2)_n CH_3$), cyano ($-C\equiv N$), carboxylic ($-COOH$), and sulfonic acid ($-SO_3H$) (43). In addition to being auxochromes, amino ($-NH_2$), hydroxy ($-OH$), and alkoxy ($-O-R$, $R =$ alkyl) groups are electron donating groups which increase fluorescence intensity (3,22,42,69,71,91). Electron withdrawing groups, such as nitro ($-NO_2$) and azo ($-N{=}N-$), decrease fluorescence intensity as do sulfonic acid groups which frequently are incorporated on FWA compounds to increase water solubility (3,22,69,71,91). Fluorescence intensity also is influenced by the dipole moment of the molecule (91). For example, if an electron donating group and an electron withdrawing group are mutually in the para positions on a benzene molecule, the dipole moment is increased and the intensity of the fluorescence is decreased. However, if two donating groups are in the para positions, the dipole moment is small and the fluorescence intensity increases.

The suitability of a fluorescent substance to be used as an FWA depends on the wavelength shift between absorption and emission. The most desirable wavelengths of maximum absorption are around 350 nm (in solution) to correspond with emitted light around 450 nm (77). This would result in emitted light in the blue to blue-violet range which is necessary to rid the substrate of its inherent yellow hue. With dominant absorption shorter than 335 nm, a blue-violet hue will result upon emission; and longer than 365 nm, a greenish blue fluorescence occurs (3). Ideally, FWA's should absorb no visible light, yielding themselves colorless. Most do possess a yellow color which only becomes apparent at high concentrations on the substrate (6,87). For every FWA and substrate there is an optimum concentration range beyond which there is a decrease in the observed whitening effect, even though the fluorescent effect often continues to increase when determined instrumentally (54,88). When the concentration is such that all the incident ultraviolet radiation is absorbed, a further increase in concentration only builds up the inherent yellow color of the FWA.

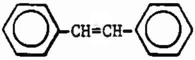
For a substance to fluoresce the incident light source must contain ultraviolet radiation which can be absorbed by the molecule and converted to visible light. If ultraviolet radiation is absent in the light source, no fluorescence will occur. Natural and artificial light sources vary in the wavelengths and intensities of ultraviolet radiation present. Of the sun's radiation which reaches the earth, approximately 40% is visible light, 5% is ultraviolet radiation, and the remaining is infrared radiation (57,77). Many other artificial light sources such as fluorescent lamps contain the ultraviolet radiation which is necessary for a substance to fluoresce.

Classification of FWA´s

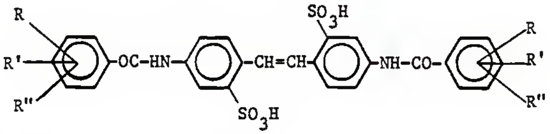
As previously discussed, both the parent chemical structure and auxochromic groups on the FWA molecule influences its end use, method of application, substrate affinity, and fastness properties. The major chemical classes of FWA´s that have commercial importance are derivatives of stilbene, coumarin, carbostyril, triazole, pyrazoline, naphthalimides, benzoxazole, and benzimidazole.

Stilbene

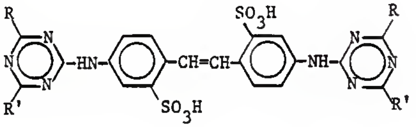
The most important class of FWA´s are derivatives of stilbene (29). They are components in over 80% of the commercial products used for finishing textiles and are incorporated into detergents to improve fabric whiteness (42,44). The basic structure of this class of compounds is shown below.

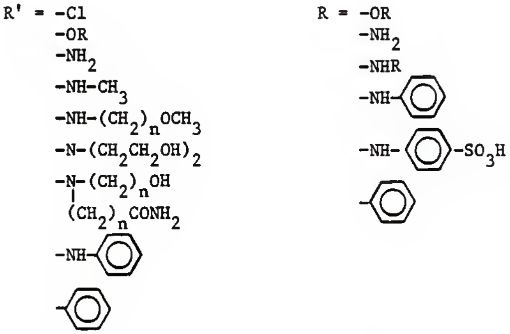


A variety of derivatives are possible within two specific groups. The first are simple stilbene derivatives of 4,4´-diaminostilbene-2,2´-disulphonic acid. A typical structure is shown below.



The second group of stilbene structures are those of the 4,4´-diaminostilbene-2,2´-disulphonic acid type acylated by cyanuric acid which are referred to as triazinyl stilbenes. FWA's of this type are of leading importance commercially because of their relatively low cost, high brilliance, and satisfactory fastness properties on cellulosics and polyamides. However, in solution they are not resistant to bleaching agents containing chlorine (44). They can be applied to cellulose and polyamide textiles by exhaustion methods or pad applied in conjunction with easy-care resin finishes. In addition, they frequently are added to detergents to whiten cellulose and polyamide fibers, and they are the only FWA used on paper (43). The general structure and important substituent groups are shown below.





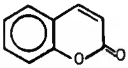
$R' = -Cl$
$-OR$
$-NH_2$
$-NH-CH_3$
$-NH-(CH_2)_nOCH_3$
$-N-(CH_2CH_2OH)_2$
$-N(-(CH_2)_nOH)-(CH_2)_nCONH_2$

$R = -OR$
$-NH_2$
$-NHR$

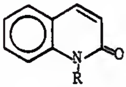
The type and complexity of the R group influences the wavelengths of maximum absorption of the FWA as well as its substantivity for specific fiber types. For example, as the R group becomes more complex, the wavelength of maximum absorption of the FWA (in water) is shifted progressively longer from 346 nm to 358 nm. The introduction of an NH_2 group to the triazinyl stilbene structure shifts the absorption bathochromically (from red to blue) (43). Acylation of 4,4´-diaminostilbene-2,2´-disulfonic acid with cyanuric acid shifts absorption from 340 nm into a more favorable absorption range of 345-352 nm. At the same time the affinity for cellulose and polyamides is increased by the cyanuric acid group (43). FWA´s based on the above structures are used in detergents and for cellulosic and polyamide fibers by exhaustion methods. The more complex structures are incorporated into the polymer melt during polyester manufacturing.

Coumarin and Carbostyril

The second major chemical class of FWA´s includes coumarin and carbostyril compounds which are represented by the following general structures.

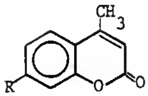


Coumarin



Carbostyril

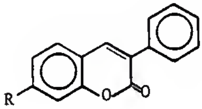
FWA´s within this class are used in polyacrylonitrile, polyamide, acetate, triacetate and polyester spinning solutions, plastics, and detergents. The 7-aminocoumarin derivatives are used to whiten polyamide fibers, however, they are less desirable than the stilbene type FWA´s due to their undesirable wavelength shift and inferior lightfastness (29,43). Typical FWA's of the 7-aminocoumarin type are shown.

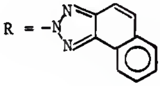


R = $-N(CH_3)_2$

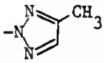
$-N(CH_2CH_3)_2$

Polyester fibers are whitened with water insoluble derivatives of 3-phenylcoumarin such as the FWA's shown below. The wavelength of maximum absorption for the compounds (in DMF) are included.

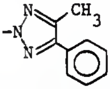




λ max = 375 nm

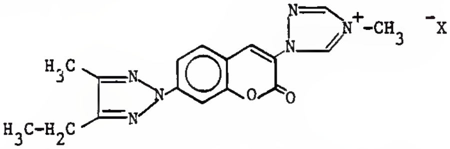


λ max = 352 nm

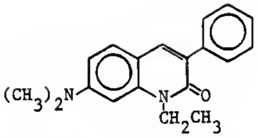


λ max = 359 nm

Water soluble coumarin derivatives, such as the one below, are used to whiten acrylic fibers.



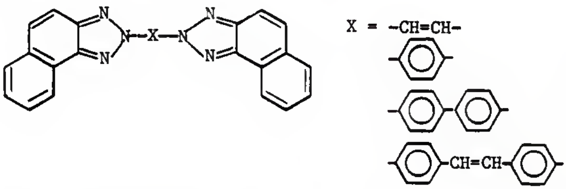
Carbostyril derivatives have limited use but are found in FWA's for polyamide fibers. These compounds usually are 7-amino derivatives of carbostyril and are applied from alkaline wash liquors. One such structure is shown below.



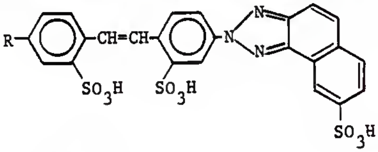
Derivatives of both stilbene and coumarin offer maximum variability in absorption range of the FWA in contrast to the other FWA chemical types. Auxochromic substituents can be changed to obtain the desired whitening effect. The possibility of variation is less in the other chemical types because the structure itself already absorbs in the range necessary for it to serve as an FWA.

Triazole

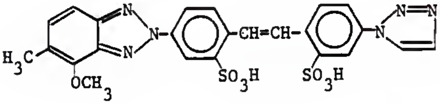
Triazole FWA's were developed while manipulating the triazinyl stilbenes in an attempt to obtain a structure which was resistant to chlorine bleaches but which still had outstanding brilliance. It is not necessary that they be derived from stilbene, but experience has shown that the stilbene compounds are the most valuable because they possess the best lightfastness (44). The general structure of this class of compounds is given below.

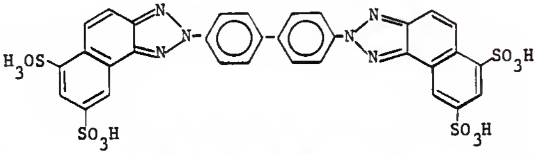


Numerous derivatives of triazole are possible, with this class being characterized by a 5-membered ring containing 3 nitrogen and 2 carbon atoms. As the number of 6-membered conjugated rings on the molecule increases, the wavelength of emission becomes longer, shifting further into the visible spectrum from blue to green. Water soluble compounds of this type are suitable for whitening cellulosic and polyamide fibers. Some typical structures are shown below.



R = -H
-NH-CO-R

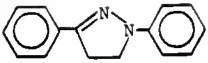




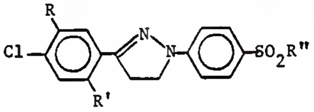
When FWA's of the triazole series are used together with chlorine bleaches, the brightening effect often is increased considerably and the brilliance is greater than that which is attainable with an FWA alone. However, no explanation has been given to explain the mechanism of this synergistic effect (44).

Pyrazoline

FWA's within the pyrazoline chemical class are derivatives of 1,3-diphenyl- 2-pyrazoline as shown below.



Because this compound already absorbs in the appropriate range for FWA's, only minor changes to the molecule are necessary, such as chlorine substitution in the 3-phenyl nucleus which results in the most favorable absorption range. Substitution into the 1-phenyl nucleus by an SO_2 group increases affinity for certain substrates without altering the fluorescence properties. Several major structural types of pyrazoline compounds are shown below.

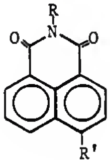


	R	R'	R"
a)	-H	-H	$-NH_4$
b)	-H	-H	$-NH(CH_2)_3-\overset{+}{N}-(CH_3)_3 \quad {}^{-}O_3SOCH_3$
c)	-H	-H	$-CH_2CH_2SO_3H$
d)	-H	-H	$-CH_2CH_2O\underset{\overset{\mid}{CH_3}}{C}H-CH_2N(CH_3)2$
e)	-Cl	$-CH_3$	$-CH_2CH_2SO_3H$

Structural variations in pyrazoline compounds have a considerable influence on their use, although the wavelength of maximum absorption (in water or methanol) varies just slightly from 364-367 nm. For example, structure (a) is applied to polyamide textiles by exhaustion from an alkaline wash liquor, whereas (b) is a cationic FWA used on acrylics. Structures (c) and (e) can be applied by exhaustion to polyamides from an acid bath or by continuous methods, while (d) is a water insoluble FWA for acrylics. Other textile fibers such as acetate and triacetate are also whitened with FWA´s of this type.

Naphthalimide

Derivatives of naphthalimide can be used for a large variety of materials such as acetates, acrylic, olefin, and polyester and are usually applied in finishing. The general structure and several FWA´s within this class are shown below.

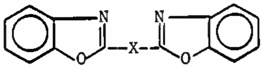


R = $-CH_3$
$-(CH_2)_nCH_3$
$-(CH_2)_3\overset{+}{N}(CH_3)_3$

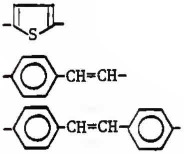
R' = $-OCH_3$
$-O-R$
$-SO_3H$
$-NHCOCH_3$

Benzoxazole

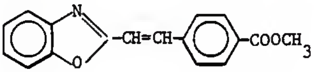
The most extensive research and development work has been carried out on benzoxazole compounds, accounting for almost a quarter of the entire technical literature in this field (43). The general structure is shown below.



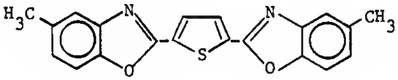
X = -CH=CH-



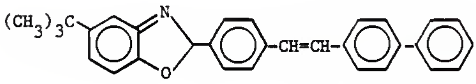
The X consists of a variety of double bond systems such as ethylene, thiophene, phenylethylene, or stilbene. As conjugation increases, absorption is shifted to longer wavelengths. These FWA´s are important for polyester, acrylic, acetate, triacetate, and plastics. They may be applied to polyester and polyamide fibers in the spinning solution or as water insoluble dispersions. Some typical examples are shown below along with the wavelength of maximum absorption (in DMF) (43).



λ max = 342 nm



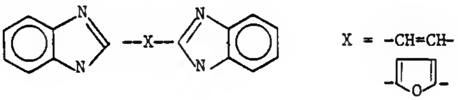
λ max = 358 - 395 nm



λ max = 365 nm

Benzimidazole

Derivatives of benzimidazole are used in detergents for improving the whiteness of cellulosic and polyamide fibers. They also are used in finishing and mass whitening of acrylic fibers. The basic structure of benzimidazole FWA´s are shown below.



Selection and Application of FWA´s to Textiles

FWA´s also are categorized according to application class as are dyestuffs. The application classes of FWA´s suitable for specific fiber types are as follows:

Fiber Type	FWA Application Class
Cellulosic	Direct, Reactive
Acrylic	Basic, Disperse
Acetate/Triacetate	Basic, Disperse
Nylon	Acid, Basic, Disperse
Polyester	Disperse

A particular application class may contain several chemical classes of FWA´s, and generally refers to the application conditions and/or method of association with the fiber. Numerous studies (5,8,26,54,64,71,73,88) have investigated the application conditions and factors that influence an FWA´s ability to yield bright whites, such as type of substrate and the presence of other chemicals or finishes on the fabric or in the treatment bath.

Surface Application Methods

FWA´s can be applied by a variety of batchwise and continuous methods, depending on fiber type, whether yarn or fabric is being treated, general manufacturing sequence, and application procedures suitable for specific FWA´s (64,73). They often are applied in conjunction with other treatments, such as during scouring, bleaching, or heat setting. Exhaust procedures employ batchwise equipment such as winches, jigs, or beam dyeing equipment, whereas pad-thermosol and pad-steam techniques are used in continuous processing. Many whiteners can be applied by either an exhaust or pad-application procedure. Research has shown, however, that a given whitener applied by exhaustion will yield better whiteness values than when applied by a pad method (20,54).

Important variables to be considered when applying FWA´s depend primarily on application class, fiber type, and method of application. Direct type FWA´s are most commonly applied to cellulose fibers by exhaustion, such as from a bleach bath, but they also may be applied by pad application procedures. The degree of substantivity, rate-of-strike, and application conditions (i.e. presence of electrolytes and temperature) determine the appropriate application method for direct type FWA´s on cellulosic fibers. Within this application class, FWA´s with low-substantivity and a slow rate-of-strike would be suitable for pad application methods. When using exhaustion techniques, a fast rate-of-strike FWA with high-substantivity would generally be more suitable except in some applications such as package dyeing. Electrolytes and elevated temperatures can be used to increase the exhaustion of some direct type FWA´s with low-substantivity and a slow rate-of-strike. In the application of high-substantive FWA´s, control of temperature can increase levelness, whereas the application of low-substantive types, temperature is less critical and only has a small effect while electrolytes are more effective in promoting exhaustion. Salt is used to decrease the negative charge on the fiber, thus allowing the FWA and cellulose to have greater affinity so that hydrogen bonds between them can be formed.

Reactive type FWA´s can be applied to cellulosic and polyamide fibers. This class of FWA´s usually contains a triazine ring in their molecular structure which covalently bonds with the fiber to give excellent washfastness. Alkaline conditions are necessary to facilitate the reaction between the FWA and the fiber. Application temperatures may need to be carefully controlled for best results, depending on the reactivity of the FWA molecule, and salt is used in the bath to aid exhaustion. In general, reactive type FWA´s are known for their outstanding brillance, ease of application, and high exhaustion, but they lack resistance to chlorine bleaches in the application bath.

Anionic (acid) type FWA´s are applied to polyamide fibers by exhaustion in the scouring process or by padding in a continuous operation. The pH of the bath often influences the chemical stability, solubility, and affinity of the FWA for the substrate (54). Depending on the specific FWA, a neutral to acidic pH may be used. Anionic FWA´s form salt linkages with the fiber. Selected direct type whiteners with anionic water solubilizing groups also can be applied to polyamide fibers, forming salt linkages similar to acid types.

Disperse type FWA´s are most commonly applied to polyamide and polyester fibers. These FWA´s are dispersed within the fiber by thermosoling after pad application or by exhaustion methods at the boil. Carriers often are used to increase exhaustion when the FWA is applied under atmospheric conditions, however, they are not needed if the exhaustion temperature is raised above the boil (to about 130°C).

Condition of the Substrate

The effectiveness and efficiency of the FWA also is influenced by fabric preparation (i.e. purification) prior to the application. The percent add-on for a particular FWA will be similar for unbleached, partially bleached, and fully bleached fabrics, but the difference in the apparent whiteness is substantial. The whitening effect imparted by the FWA usually is proportional to the amount of bleaching during fabric preparation (87,88). FWA´s usually reduce the amount of chemical bleaching needed to achieve a desired level of whiteness, however, they can not replace chemical bleaching. Furthermore, the whitening effect of FWA´s may not be perceivable on unbleached fibers, such as cotton, that are quite beige or yellow because the blue wavelengths are absorbed by the yellow color of the substrate. When the majority of the yellow color is removed by bleaching, the increase in the reflectance of blue light is perceivable. In most instances, the amount of yellow color removed is proportional to the extent of chemical bleaching. However, there is a point where any further bleaching will only remove a very slight amount of the remaining yellow color and increase the potential of chemical degradation of the substrate. Hence, FWA´s are used to compensate for the residual yellowness remaining after chemical bleaching.

Influence of Other Chemicals

Other chemicals present on the fabric such as finishes, whether they are applied prior to, in conjunction with, or subsequent to the application of the FWA, can have a pronounced effect on the whiteness obtained. For example, resin finishes used to impart crease resistance or permanent press properties to fabrics often require acidic or metallic catalysts which can substantially reduce the whitening effect of a FWA (87). Softeners applied in conjunction with resin finishes also can reduce the effect of a FWA, especially if they are not similar ionically. A slight dulling also may occur due to the fatty portion of the softener (87).

Mass Whitening

The addition of FWA's directly to the polymer melt or solution during the fiber spinning process is referred to as mass whitening. This technique is commonly used to whiten rayon, acrylic, and modacrylic during solution spinning, and polyester and polyamide during melt spinning (18,70,77). It is particularly suitable for large production batches and reduces the need for an additional finishing step. FWA's applied by mass whitening possess better intrinsic whiteness and yield more brilliant colors after dyeing, however, it is important that the concentration of the FWA be controlled to maintain a blue fluorescence (25).

In melt spinning, FWA's can be added in the polymerization stage, but they must be chemically and thermally stable to withstand the high temperatures involved in production, and they must not contain functional groups that could react with the polymer or additives. Incorporation of the FWA into the polymer chain is possible provided that it has a suitable chemical structure. This can be accomplished by methods such as transesterification. If a discontinuous manufacturing process is used, FWA's also can be added to the polymer chips before they are melted and extruded (24,25,32). FWA's applied in the melt must not be volatile or sublimate from the melt in a vacuum (15,77). FWA's applied during the melt spinning stage usually have no adverse effects on the polymer properties (i.e., viscosity or melting) or on the physical properties of the fiber (24,32). However, mass whitened fibers often exhibit an appreciable increase in breaking extension, as well as a slight decrease in tenacity. This has been attributed to the plasticizing effect of the FWA (24).

The two methods of solution spinning are wet spinning and dry spinning in which a solution of polymeric material is extruded into an aqueous bath or a dry atmosphere, respectively. In both methods, the FWA can be added to the solution preparation tank or injected as a concentrate into the solution prior to extrusion. FWA's applied in solution spinning must be soluble in the solvent used to dissolve the raw materials. In wet spinning, however, the FWA should be insoluble in the regeneration bath. Just as in melt spinning, the FWA should be thermally stable and chemically stable in the presence of solvents. Gel-phase whitening also is used for fibers produced by wet spinning methods. The whitener is applied from a solution by diffusion into the fiber which is still in gel form.

Other End Uses for FWA's

Today, FWA's are used in many industrial and domestic applications, including plastics, detergent formulations, photographic emulsions, leathers, furs, cosmetics, dentures, waxes, postage stamps, legal tender, documents, and food. The major end uses for FWA's include detergent mixtures, accounting for approximately 40%; paper, 30%; textile finishing, 25%; and synthetic fibers and plastics, 5% (91). The other end uses account for only a minimal amount of the total volume produced.

Detergents

The apparent efficiency of detergents is increased by the use of FWA's because of their ability to mask colored impurities and increase fabric whiteness. Advertising slogans such as "Whiter than White" were successful in selling detergents which contained FWA's (18). The main factor that determines the type of FWA used in detergents is the composition of the laundry load. Because of the commercial significance of cotton and its inherent yellow color, it is those brightening agents suitable for cotton that usually are added to washing powders (18,91). Other types used to brighten polyamides, acetate, triacetate, and acrylic also may be added. Whiteners for polyesters are added less frequently to detergents because of the low temperature (below 100°C) used in washing. Since surface whitening of polyester requires temperatures of about 120°C, only minimal whitening would be possible from detergents. Many of the synthetic fibers are mass whitened and, therefore, surface whitening obtainable from detergents is less important.

In addition to composition of the wash load, other factors that are important to the selection of an FWA for a detergent include composition of the detergent, laundering conditions, lightfastness, interactions of one FWA with another, hue, price, availability, and dermatalogical properties. With respect to detergent composition, the most important criteria is the ionic nature of the surfactant system. For example, some anionic type FWA's are more effective in anionic systems than in nonionic systems, while other anionic FWA's may be suitable in both systems (77). Because many FWA's for cellulosic fibers require salt to facilitate exhaustion, appropriate fillers are added to the detergent formulation (91).

Laundering conditions also influence the amount of FWA absorbed by the fiber. Conditions range from hand washing in cold water to machine washing almost at the boil. The liquor-to-goods-to-detergent ratios and the use of hypochlorite bleaches also differ. Some FWA's are unstable to hypochlorite bleaches and, therefore, suitable selections must be made. Often a combination of FWA's are used which are effective under different laundering conditions and on various fiber types. The concentration of FWA in a detergent depends on the laundry conditions used in the location where the detergent is marketed. In the United States, approximately 0.3–0.5% or more of the weight of a detergent is a FWA. The amount drops to 0.1–0.3% or less in Western Europe and as low as 0.05–0.2% in other parts of the world (77).

Problems Encountered with FWA´s

Washfastness

The washfastness of a FWA depends on its affinity for the fiber and the method of FWA-fiber association. They are bound to fibers by a variety of methods, as previously described, depending on the fiber substrate and molecular structure of the FWA. Those reacting with the fiber through covalent bonds or that are physically entrapped within the fiber have the best washfastness, whereas those associating by hydrogen bonding usually have the poorest washfastness. The affinity of the FWA for the substrate often determines the method of application. Low-substantive types applied by padding will have poor washfastness, compared to high-substantive types applied by exhaustion. However, the FWA usually is pad applied with other finishes such as resin precondensates which improve their washfastness (8).

As mentioned previously, FWA´s are added to laundry detergents to replace or regenerate the whiteness of textiles because of the poor washfastness of some FWA´s applied in finishing. However, their presence in detergents can create other problems. When colored garments are washed in detergents containing a FWA, an undesirable color change can occur due to the addition of blue light to the reflectance curve of the dyed fabric. The alteration in color may be falsely attributed to poor washfastness of the dye, especially in pastels. To eliminate complaints arising from changes in color, it has been suggested that FWA´s also be applied to textiles that will be dyed (59).

Lightfastness

Factors Influencing Lightfastness

An important factor in the selection of a FWA for a particular end-use is its lightfastness or ability to retain its whitening effect during light exposure. The first compounds developed had poor lightfastness and often resulted in colored decomposition products on textile fibers (2). Today, commercially important FWA's generally have moderate lightfastness and do not discolor during light exposure. It is not suprising that their lightfastness is only moderate, since they primarily absorb high energy ultraviolet light and are applied at such low concentrations. The same factors that influence the lightfastness of dyes also influence the lightfastness of FWA's, such as the physical and chemical nature of the dye and substrate and exposure conditions such as light source, temperature, humidity, and atmospheric contaminants (7).

The physical state of the dye or substrate is one of the most important factors which influences fading. Dyes and FWA's are applied at various concentrations to textile substrates, however FWA's generally are applied in lower concentrations than dyes, and this must be considered when comparing their lightfastness to that of dyes (8). As the concentration of dyes or FWA's is increased, the lightfastness usually improves (41,55,59,61). With increasing concentration there is a greater chance for large clusters of molecules, called aggregates, to form inside the fiber. When aggregates are present, there is less dye or FWA molecule surface available for exposure to light, air, and moisture and, therefore less fading. In some instances, however, an increase in concentration of a FWA or dye can decrease lightfastness (12,41). This is known as anomalous fading and contradicts the aggregation effect.

The physical nature of the substrate to which the dye or FWA is applied also influences lightfastness. As previously discussed, dyes often exhibit greater lightfastness on those hydrophilic fibers that have high moisture regains. These fibers tend to have a greater proportion of amorphous regions which facilitates the formation of larger dye aggregates (39). The opposite applies when evaluating the lightfastness of dyes on hydrophobic fibers, with lightfastness decreasing as moisture regain of the fiber increases because moisture in the fiber substrate often accelerates fading. The dye or FWA molecule also tends to be dispersed within hydrophobic fibers, rather than just on the surface, which improves the lightfastness properties.

Limited research is available which evaluates the lightfastness of FWA´s on specific fiber types, however, generalizations regarding certain fibers can be made. The lightfastness of FWA´s on cotton is poor to moderate, and the decomposition products may be slightly colored (27). However, the yellow discoloration that occurs may be attributed to the disappearance of the fluorescence, rather than to colored decomposition products (70).

The lightfastness of FWA´s on wool has been studied more than any other fiber because of its inherent beige color even after bleaching. It is often difficult to obtain a permanently white wool with reduction type bleaching agents because it naturally oxidizes back to its original color. This photochemical process is accelerated by the application of a FWA which acts as a photosensitizer for the yellowing of wool proteins (12,52,64,67,84). The lightfastness of the FWA on wool has been increased by confining the FWA within a polymer applied to the wool (47,49,50,61). However, the increased whitening is still temporary due to yellowing of the resin, but it does suggest that a bright, white wool could be obtained if a suitable resin and FWA could be found (49).

Limited research is available on the lightfastness of FWA's applied to other fiber types such as polyester and nylon. The lightfastness of FWA's applied in the mass to films and fibers varies, depending on the polymer and FWA used (68). For example, when FWA's were applied to both acrylic and polyester by exhaustion methods and exposed to light, an increased whitening effect or bleaching occurred. As exposure continued, however, the FWA on the acrylic became yellow, while the acrylic fiber itself remained white (55), and the polyester fiber returned to its original color (59). FWA's also have been applied by exhaustion methods to nylon fibers. Upon exposure to light the fiber tended to yellow which was attributed to loss of the FWA. However, the fibers also showed a slight yellowing beyond that which naturally existed in the fiber (70). Additional research is needed on the lightfastness of FWA's applied to synthetic fibers.

The chemical nature of the dye or FWA and substrate has less of an effect on lightfastness than the physical state (59). Light is readily absorbed by highly conjugated systems found in dyes or FWA's. When the electrons become excited, the molecule is unstable and very active, and the electrons may react with anything that comes into contact with them such as oxygen or the fiber. The dye or FWA molecule may then be decomposed which would appear as fading. A dye or FWA molecule can be represented in two parts, i.e., the nucleus which is characteristic of a particular dye or FWA class and the substituent groups which are present on the nucleus (34). The nucleus seems to determine the overall lightfastness of a dye or FWA chemical class, while the substituents alter the lightfastness properties of a particular molecule within a class. Research has shown that symmetrical dye molecules exhibit greater lightfastness than those that are unsymmetrical (34,39). Furthermore, amino ($-NH_2$), hydroxyl ($-OH$), methyl ($-CH_3$), and methoxy ($-OCH_3$), or thiol ($-SH$) groups on dye molecules often decrease lightfastness properties, while nitro ($-NO_2$), sulfonic ($-SO_3H$), and carboxyl ($-COOH$) groups and chlorine or bromine atoms increase lightfastness (34,39). In several dye classes, an electron withdrawing group, such as a nitro, sulfonic or carboxylic acid, in a meta position from an electron donating group on a benzene ring decreased lightfastness, but lightfastness could be improved slightly by changing the withdrawing groups to a para position. Further improvements were made by changing the group to an ortho position (34,39). Research on how substituent groups on FWA molecules alter lightfastness is limited. However, alkyl and alkoxy (especially methoxy) groups and chlorine atoms have been found to increase the lightfastness of many FWA´s (35)

The various conditions under which a textile may be exposed to light, such as the type of light source, humidity, temperature, and atmospheric contaminants may appreciably influence the lightfastness of FWA's and dyes. The presence of oxygen or moisture around the substrate during exposure usually increases fading. High moisture or humidity is thought to swell some fibers allowing oxygen to reach the dye molecules, accelerating the fading reaction. High temperatures during light exposure increase the rate of chemical reactions and may influence fading in the same manner.

The light source, its spectral distribution, and intensity are very important in lightfastness. The amount of fading which occurs often is proportional to the intensity of light (7,22). In addition, radiation in the ultraviolet region tends to cause the most fading. Daylight contains approximately 5% ultraviolet radiation, fluorescent lamps approximately 3%, and incandescent lamps emit less than 1% ultraviolet light (57,77).

Lightfastness of FWA's in Solution

Stock solutions of FWA's often are used in preparing textile finishing baths, and the majority of FWA's are applied from aqueous solutions as are a multitude of other finishing chemicals. However, FWA's in solution are sensitive to the absorption of UV light which can influence their lightfastness. If aqueous solutions of FWA's are exposed to UV light for extended periods, their ability to fluoresce may be decreased substantially (59,67,70,72). The FWA can no longer fluoresce due to a conversion from the fluorescent trans configuration to the non-fluorescing cis configuration, with an equilibruim of the cis and trans isomers forming in the solution. Continued exposure to ultraviolet radiation gradually causes the FWA to decompose, especially in stilbene type FWA's (59,67,72). Singlet oxygen may contribute to the decomposition of stilbene and other chemical type FWA's in solution (67,72). Manufacturer's technical literature which accompanied the FWA's obtained for this study stated that stock solutions should not be used in applying the FWA, or if stock solutions were prepared, they should be used immediately.

Effect of FWA's on the Lightfastness of Dyes

FWA's also are applied to goods that are to be dyed pastel shades to produce crisper, brighter colors. However, because FWA's increase the absorption of ultraviolet radiation, which is known to increase the fading of dyes, they may accelerate dye fading. On the other hand, the FWA also may protect the dye by absorbing the incident ultraviolet light. Both increased and decreased fading of dyes has been found to occur with FWA's. For example, the protective properties of the FWA on reactive dyes varied with the type and concentration of FWA and the presence of other finishing agents (31). Lanter (59) found the lightfastness of vat dyes appeared to be reduced when applied in combination with an FWA on the fabric because a change in hue occurred upon exposure to light. However, once the FWA had faded, the dye exhibited its usual color and fastness characteristics. Other researchers (1,40,82,89,90) have reported that the lightfastness of dyes decreased due to the application of FWA's. When this occurred the dye appeared to be serving as a quencher, decreasing the fading of the FWA as well (1,89,90).

Fiber Degradation

Factors Influencing Fiber Degradation

In addition to accelerating fading in dyes, FWA´s also can increase fiber degradation during light exposure. Fiber degradation due to light is influenced by many of the same factors as fading, and in most instances the spectral distribution and intensity of the light is of primary importance. It is the high energy, ultraviolet radiation in light sources that causes the greatest amount of chemical degradation. No energy shorter than approximately 290 nm reaches the earths surface, hence, it is the wavelengths between this atmospheric cut off and 380 nm, the beginning of the visible range, which are the most destructive (57). The mechanism by which light influences fiber degradation is varied and complex. To better understand the reaction that occurs, an indepth discussion of light and its energy is necessary.

As previously mentioned, a photochemical reaction occurs when a molecule absorbs a photon of light that has an energy greater than or equal to the difference in energy between the ground state and the excited state of the molecule. When the molecule absorbs the photon of light, the electrons become excited to a higher energy level, resulting in an unstable, active molecule which can dissipate its energy in a variety of ways, including heat production, transfer of the energy to other molecules, and bond breaking (86). Chemical bonds may be broken if the energy absorbed initially by the molecule is greater than the energy holding the chemical bonds together in the molecule.

The absorption of a photon of light can occur through a variety of reactions. Photodegradation of fibers may occur by either direct photolysis or photosensitization. Direct photolysis occurs when chromophores, present in the repeat unit of the fiber's polymer chain, absorb the damaging ultraviolet radiation, causing direct rupture of chemical bonds. In cellulose the cleavage of either the carbon-carbon or carbon-oxygen bonds will require energy of 75-80 kcal/mole (3.13 to 3.34 x 10^5 joules/mole) and the carbon-hydrogen bonds, 85-100 kcal/mole (3.56 to 4.18 x 10^5 joules/mole (21). Light of 400 nm wavelength is equivalent to 71 kcal (2.97 x 10^5 joules), 300 nm to 95 kcal (3.97 x 10^5 joules), and 200 nm to 143 kcal (5.98 x 10^5 joules) (21). If ultraviolet radiation with a wavelength of 340 nm or shorter is absorbed by the cellulose molecule, the energy for direct photolysis will have been provided (21,33,75,83). However, some polymer repeat units such as polypropylene, contain no chromophores on the backbone, and yet degradation readily occurs. This is due to impurities present in the polymer, including dyes, FWA's, and finishes, which also contain chromophores. This type of fiber degradation is referred to as photosensitization (86). The impurities absorb the photon of energy, become excited and then react with themselves, the atmosphere, moisture, or the fiber (21,33).

The changes that occur in fibers may include free radical-induced chain scission, oxidation which introduces carbonyl or carboxyl groups into the polymer and which also may break the polymer chain, formation of chemical bonds between different molecules (crosslinking), the formation of unsaturated molecules or the disappearance of unsaturated groups, and/or probably many other reactions (45,78). For example, the changes that occur in cellulosic fibers after exposure to light include increased yellowing, decreases in polymer chain length, increase in solubility, and formation of functional groups such as carbonyl and carboxyl groups (21,34,75). The effect of light is evaluated by changes in mechanical properties such as breaking strength, elongation, and fluidity measures; by the detection of functional groups formed such as carbonyl or carboxyl groups; and by stains or titration techniques (66).

Fiber Degradation due to FWA´s

Fiber degradation resulting from the application of FWA´s has received little attention by researchers, compared to that attributed to dyes or degradation of the FWA itself. FWA´s applied to cotton and the regenerated cellulosic fibers have been investigated the most, but the literature is not extensive (1,21,27,70). Although researchers (1,27,70) have concluded that FWA´s do increase cotton fiber degradation, the amount ·of degradation which occurred varied due to differences in experimental variables including light source, exposure time, and FWA type, concentration, and application method. For example, trade named products often were applied, but no reference was made as to their chemical structure (1,70). In one study (27) no relationship was found between chemical structure and fiber degradation, however, it is difficult to draw conclusions when only one FWA in a chemical class was evaluated and specific concentrations applied were not given.

Hence, studies investigating the relationship between chemical structure and lightfastness of FWA´s on cotton and their potential for causing photodegradation of the substrate are needed. Furthermore, by evaluating many different structures within one chemical class, it may be possible to gain a better understanding of how functional groups on the FWA molecule influence lightfastness and fiber degradation. Application of a known quantity of FWA to the fabric, which would be equivalent to that used in actual commercial finishing, also is necessary for generalizing the results to commerical processing.

Evaluation of FWA´s

White surfaces are characterized by high reflectance (more than 50%) throughout the visible spectrum (37,46,48). In general, surfaces visually appear whiter as the intensity and uniformity of the spectral reflectance increases and absorption decreases. A variety of visual and instrumental methods have been used for evaluating the whiteness of a fabric, such as by 1) visually comparing with a set of standards, 2) determining the tristimulus values, 3) calculating whiteness or yellowness indices, and 4) recording absorbance, transmittance, or reflectance spectra. The phenomenon of fluorescence, however, greatly complicates the visual and instrumental assessment of whiteness because the amount of light reflected from a fabric treated with a fluorescent compound often exceeds 100% of the incident light. In addition, the spectral distribution of the light source, especially in the UV region, the personal preference of the observer or the sensitivity of the instrument greatly influences quantitative assessment of whiteness as well as the ability to correlate visual and instrumental data (4,23,46). An understanding of the visual and instrumental methods of evaluating the whiteness of fabrics treated with fluorescent whitening agents is germane to the selection of appropriate methods of instrumental analysis and data interpretation relating to the concentration, efficiency, and lightfastness of FWA´s on textile substrates.

Visual Evaluation

As mentioned previously, FWA´s increase the whiteness of a fabric by increasing the amount of visible light reflected by the substrate as a result of absorbed UV energy being re-emitted as visible radiation (13). In general, the whitening effects of FWA´s are proportional to the amount or intensity of the fluorescence emitted from the fabric (4). In practice, however, the relative whitening effect of an FWA is determined by human assessment (consumer preference) as well as by the spectral qualities of the light source and the fluorescent effectiveness of the FWA (concentration required to give a designated amount of whiteness) (4). Visual assessment of fabric whiteness is commonly employed for quality control and research purposes. However, it is considered the least precise method, especially when FWA´s of different shades are compared against each other, because shade differences confound the estimation of whiteness (4). Both consumer preference for particular hues of whiteness and the eyes greater sensitivity to longer wavelengths further complicates visual assessment. In addition, FWA´s have both a lightening and a blueing effect, the later of which has a much greater impact on visual assessment (4).

Various textile and dyestuff companies have developed standardized white scales for assessing fabric whiteness. For example, the Ciba-Geigy Plastic White Scale (CGPW Scale) consists of melamine plates with corresponding whiteness values ranging from -20 to 210 (62).

Visual evaluations may be conducted in daylight or under UV illumination, the later of which is considered more precise for FWA build-up and lightfastness studies. However, visual methods of assessment usually are unsuitable for comparing the fluorescent efficiency of different FWA's (4). In addition, the spectral distribution of the illumination source, especially in the UV region, is extremely important in evaluating fluorescence and often determines the relative effectiveness of the FWA at a given concentration (4).

Instrumental Evaluation

Instrumental methods of evaluating whiteness and fluorescence have become more prevalent than visual evaluations because they are more precise and discriminating (62). However, many of the methods commonly used to measure the whiteness of nonfluorescent whites may not be suitable for comparing some FWA's, such as conventional tristimulus colorimetry and absorbance/reflectance spectroscopy.

One of the simplest instrumental methods for evaluating the whiteness (W) of textiles is based on the reflectance value (R) at one wavelength (i.e. 460 nm) in the blue region of the visible spectrum

(W=R) (46,48). Other whiteness calculations are determined by measuring the reflectance of the sample at two wavelengths (blue and red regions), as is illustrated by Stephansin´s whiteness formula $[W=R_{430}-(R_{670}-R_{430})]$ (46). Similar whiteness formulas (one number whiteness indices, WI) are based on X,Y,Z tristimulus values or L,a,b color systems such as those developed by Hunter (WI=L-3b) and Stensby (WI=L+3a-3b) by using a suitable colorimeter (11,37,46,53,56,62). Many of these whiteness scalss apply a weighting factor to the blue (b) component since it has a greater influence on the relative whiteness as perceived by human subjects. The "b" dimension often is considered to bs three or four times more important than the "L" dimension (53). The whiteness index recommended by ASTM is defined as the reflectance difference WI=4B-3G, where B=Z/1.18103 and G=Y (11). Many of the whiteness scales available were developed to correlate with the visual sensation of whiteness (46).

Some of these whiteness formulas are unsuitable for measuring the whiteness of fluorescent samples due to variations in the proportion of UV wavelengths in the illuminant, especially when comparing the efficiency of different types of FWA´s. The spectral distribution of the light source influences the whitening effect of the FWA and the ability to compare fluorescent samples treated with FWA´s that have different excitation and emission characteristics (37). Attempts have been made to compensate for variations in the spectral distribution of the light source in tristimulus colorimeters such as by using special filters to attenuate either the UV or the visible part of the irradiant (46). Furthermore, new whiteness formulae have been developed which contain adjustable parameters that can be varied, depending on the whiteness bias of the subjects (46).

In addition to compensating for variations in the spectral qualities of the light source, standard illuminants have been proposed for colorimetric evaluation of FWA´s as an alternative to Standard Illuminant C (represents average daylight from total sky) which is the most widely used light source in appearance evaluation (53). Specifically, the D65 series of illuminants contain a greater amount of UV radiation in the 300–400 nm region. According to Hunter (53), the most critical factor influencing the colorimetric evaluation of FWA´s is the ratio of energy emitted by the light source in the range of maximum absorption of the brighteners (350–400 nm) to the energy in the range of maximum emittance (400–450 nm).

In conventional UV/visible spectroscopy, the transmittance, reflectance, or absorbance of a sample irradiated with monochromatic light is recorded at the specified wavelength for the incident radiation (37). For fluorescent samples, however, the relative intensity of the reflected or transmitted radiation is increased by the polychromatic power of the emitted fluorescence. The fluorescent light, which is emitted at longer wavelengths than the incident light, is inaccurately recorded at the wavelength of the incident light. In other words, the emitted or reflected radiation is detected as though it had the same wavelength as the incident energy producing an error in the curve (37,48). The more sophisticated spectrophotometers (i.e. spectrophotofluorimeters or spectrofluorometers) designed to measure fluorescence usually contain two monochrometers (or filters in simple fluorimeters) that precisely control and record the wavelength distribution and intensity of both the incident radiation and the emitted light reflected from the sample (37).

Fluorescent excitation spectra plot fluorescence intensity (emission) from the sample, at a fixed wavelength in the visible region, against the wavelength of exciting light as shown in Figure 2.

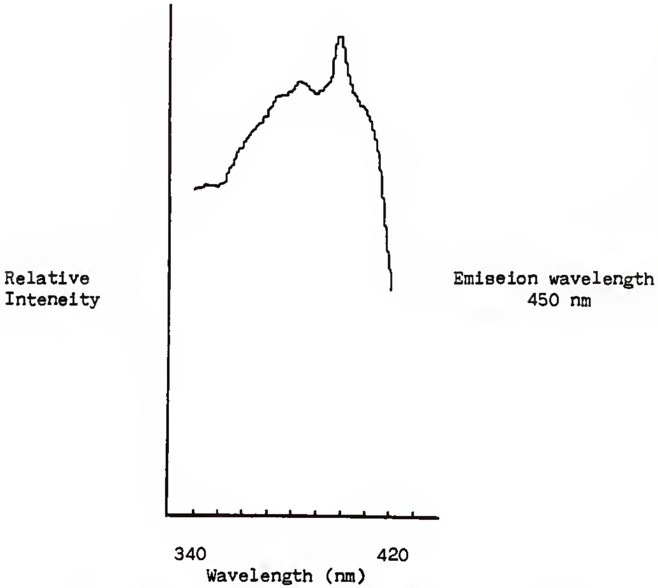


Figure 2. Fluorescence Excitation Spectrum of a Fluorescent Whitening Agent on 100% Cotton Fabric.

Hence, the excitation spectra indicates the extent to which various wavelengths of UV radiation are absorbed by the molecule.

In fluorescent emission spectra, on the other hand, the relative intensities of the various wavelengths of fluorescent light that are reflected from a FWA-treated fabric for a specified excitation wavelength of irradiation in the UV region are recorded as shown in Figure 3.

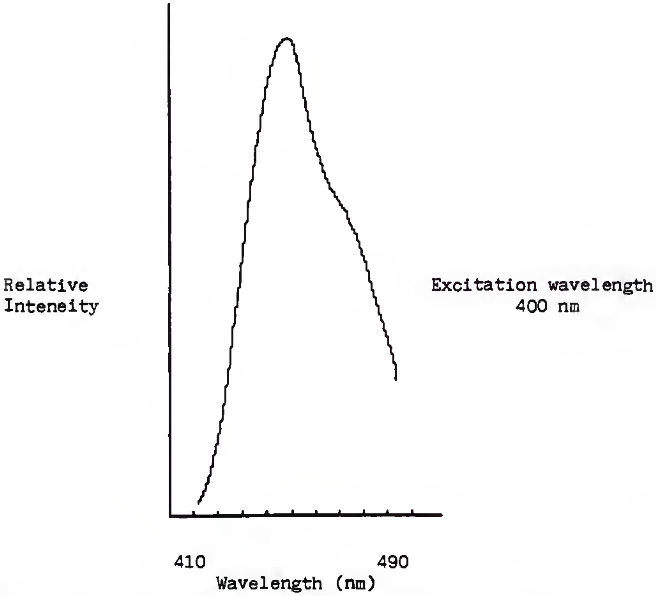


Figure 3. Fluorescence Emission Spectra of a Fluorescent Whitening Agent on 100% Cotton Fabric.

In other words, the emission across the visible spectrum is plotted against wavelength for a specified excitation wavelength, whereas the fluorescence excitation spectra indicate the wavelengths of UV radiation that are absorbed. Fluorescence spectra are used to quantitatively determine the concentration of FWA on textile substrates because emission intensity is directly related to concentration (28).

Since the intensity of fluorescence emission is directly proportional to the intensity of the incident radiation, it is important that spectrophotometric readings are adjusted for variations in lamp (i.e. xenon arc) output at specified wavelengths that occur as the lamp ages (13,62). Furthermore, corrections should be made in the spectra to account for variations in the spectral response of the detector (photomultiplier tube) which are a function of wavelength and other machine variations (13,62). Hence, corrected spectra compensate for variations in the lamp, detector, and optical components in the instrument. In the more sophisticated spectrofluorometers, the correction factors are automatically applied to the data as they are being collected, and hence the corrected spectra are readily obtained (13). These correction factors are critical when comparing the relative whitening efficiency of different types of FWA´s (62).

Other factors that influence quantitative accuracy in fluorescence spectroscopy are:

1. the instability of dilute solutions,
2. loss of substance by adsorption onto the walls of the container,
3. photo-decomposition caused by the high intensity of the incident light,
4. oxidation of fluorescent compound in solution due to the presence of oxidizing agents,

5. non-linearity in emission against concentration at high concentrations, and
6. effects of temperature and pH on the intensity and spectral characteristics of fluorescence.

The relative fluorescence efficiency of a FWA is related to the perceived whitening effect at a specified concentration. The fluorescence or quantum efficiency of a fluorescent compound is calculated by determining the quantum of absorbed UV radiation that is converted to fluorescent light in solution (i.e., the number of photons (quanta) emitted by the sample, q, per photon (quanta) absorbed, q_o, or (q/q_o) (14). Many spectrofluorometers calculate relative fluorescence efficiency, which is determined according to the following formula:

$$\text{Relative fluorescence efficiency} = \frac{E}{R-T}$$

Where:

E = emission detector, measures light emitted from a sample.
R = reflectance detector, measures light passing through a blank.
T = transmittance detector, measures light not absorbed.

The absorbed energy that is not re-emitted as fluorescence is converted into thermal energy (56). Most fluorescent compounds have a nearly constant quantum efficiency over a considerable range of incident wavelengths, however, the fluorescent efficiency decreases appreciably when the wavelengths of the incident radiation falls within the emission band (56).

Fluorescent measurements can be made on both solutions and solid samples (13). Solutions of the fluorescent compounds are placed in cuvettes, and the fluorescence which is given off equally in all directions, is collected from either the front surface of the cell, at right angles to the incident beam, or in-line with the incident beam (13). Because of the difficulties associated with measuring FWA´s in dilute solution (i.e. trans to cis conversion), they are more commonly evaluated on textile substrates. Most manufacturers of spectrofluorometers have developed solid sample holders which enable fluorescent measurements to be made on solids (paper, plastics, powders, etc.) by means of a front surface collection technique (13,74). In the Perkin-Elmer front surface accessory, incident light from the excitation monochromator strikes the sample surface at a 60° angle, and the fluorescence is detected by the emission monochromator at a 30° angle to the surface of the sample (76).

Methods for checking instrumental performance to ensure reproducibility of spectral data have been proposed by ASTM´s Subcommittee on Fluorescence Spectroscopy, E13.6, as well as in general texts on fluorescence spectroscopy (13,58,79,80,85). Routine tests for instrument linearity, reproducibility, resolution, and wavelength accuracy are recommended.

Purpose

The increasing use of FWA´s on textile items reflects their many advantages as described above. They function by absorbing UV radiation present in the incident light source and converting it to visible blue light. Hence, the addition of blue light to the reflectance spectrum of FWA-treated goods increases the perceived whiteness and brightness thereby reducing yellowness. However, FWA´s increase the potential for fading and fiber degradation because of the increase in the absorption of high energy UV radiation. The relationship between the inherent lightfastness of the FWA and its potential for causing actinic degradation in fiber substrates has not been adequately investigated. In addition, there is limited research assessing the relationship between chemical structure and pendent auxochromic and chromophoric groups on the lightfastness of FWA´s, and their potential for causing actinic degradation on fibers. Thus, the purpose of this study was to evaluate the relationship between the lightfastness of selected triazinyl amino stilbene FWA´s and their ability to induce actinic degradation in cotton.

PROCEDURE

The mechanism by which FWA's function on textile substrates (i.e., conversion of absorbed ultraviolet radiation to visible radiation) favors actinic degradation of both the compound itself as well as the textile substrate. It is well known that many FWA's have poor lightfastness which reduces their effectiveness. Similarly, they also may cause an increase in fiber phototendering because they increase the absorption of high energy electromagnetic radiation. This study investigated the relationship between the chemical structure and lightfastness properties of FWA's and their potential for causing phototendering in cotton. FWA's of known chemical structures were applied at three concentrations to cotton fabric using laboratory procedures simulating exhaustion procedures used industrially. The treated samples and untreated controls were exposed to xenon light and evaluated as to lightfastness of the FWA and phototendering induced in the substrate. Chemical structures of the FWA's also were evaluated to determine how pendent functional groups on triazinylamino stilbene compounds influenced their lightfastness and phototendering of the cotton substrate.

Experimental Fabric

This study was limited to cotton because it is an important fiber used in apparel and sheeting fabrics, both of which are major application markets for FWA's. Cotton also is one of the most common fibers whitened by surface application techniques, whereas man-made fibers are commonly whitened by adding the FWA to the polymer melt or solution during spinning (i.e., mass whitening).

A 100% mercerized cotton print cloth, style #400M, obtained from Testfabrics Inc., was used. The fabric characteristics, as presented in Table 1, were determined according to the procedures in ASTM Test Methods D3774-84, Width of Woven Fabric, D3775-85, Fabric Count of Woven Fabric, D3776-85, Mass Per Unit Area (Weight) of Woven Fabric, D1059-83, Yarn Number Based on Short-Length Specimens, and D1423-82, Twist in Yarns by the Direct-Counting Method (10).

Table 1. Yarn and Fabric Construction Characteristics of Experimental Fabric

Property	100% Cotton (Style #400M, Testfabrics)
Yarn Construction	
Warp	Z 28 tpi 34's
Filling	Z 22 tpi 37's
Fabric Count (ends x picks/inch)	83 x 73
Fabric Width	115.3 cm
Fabric Weight	106.7 g/m^2

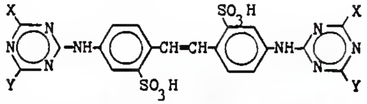
The fabrics were scoured prior to testing in a Launder-Ometer with Triton X-100 using a 30:1 liquor to goods ratio at 180° F followed by rinsing in distilled water for 10 minutes. This procedure was used to remove waxes, oils or other impurities left on the fabric that could have affected the results. After scouring, the fabrics were cut into samples measuring 25cm x 16cm and randomly assigned to the experimental treatments.

Fluorescent Whitening Agents

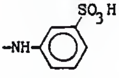
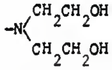
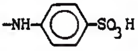
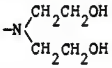
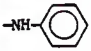
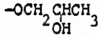
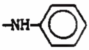
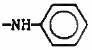
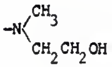
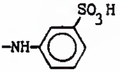
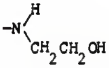
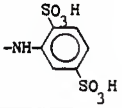
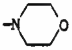
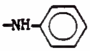
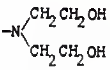
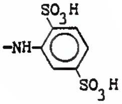
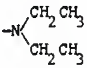
The nine FWA's evaluated are presented in Table 2. These specific compounds are commonly applied in textile finishing and from laundry detergents. They were chosen based on commercial availability, chemical structure, and ease of application. Dyebaths were prepared at concentrations of 0.05, 0.50, and 1.0% owf (on weight of fabric), by adding the required amount of fresh FWA stock solution, salt (4.0% owf), and distilled water to obtain a 30:1 liquor-to-goods ratio. The baths were placed into Launder-Ometer canisters, loaded into an Atlas Launder-Ometer, and the temperature raised to 120° F. The samples were then added and the temperature raised to 180° F and treated at this temperature for 60 minutes. The untreated controls were treated under the same conditions in a bath containing distilled water only (no salt or FWA). After treatment the samples were removed and rinsed in distilled water for 5 minutes at the same liquor ratio. The rinse was repeated again in fresh distilled water, then the samples were air dryed on a fiberglass screen in darkness for 24 hours. All work was conducted in a dimly lit room to prevent the possiblity of the FWA's converting from the trans formation to the nonfluorescing cis form.

Because of differences in chemical structure among the FWA's, the amount of FWA actually exhausting from the dyebaths was not the same. The three theoretical dyebath concentrations (0.05, 0.50, and 1.0% owf) were chosen from pilot tests so that a desirable white shade was

Table 2. Fluorescent Whitening Agents Selected for Evaluation



derivatives of 4,4´-bis-((triazin-2-yl)amino)-stilbene-2,2´-disulfonic acid

	X	Y
1. 4,4´-bis((4-(3-sulfoanilino)-6-bis(2-hydroxyethyl)amino-1,3,5-triazin-2-yl)amino)stilbene-2,2´-disulfonic acid		 $-N(CH_2CH_2OH)_2$
2. 4,4´-bis((4-(4-sulfoanilino)-6-bis(2-hydroxyethyl)amino-1,3,5-triazin-2-yl)amino)stilbene-2,2´-disulfonic acid		 $-N(CH_2CH_2OH)_2$
3. 4,4´-bis((4-anilino-6-(2-hydroxy)propoxy-1,3,5-triazin-2-yl)amino)stilbene-2,2´-disulfonic acid		 $-OCH_2CH(OH)CH_3$
4. 4,4´-bis((4-anilino-6-methoxy-1,3,5-triazin-2-yl)amino)stilbene-2,2´-disulfonic acid		$-OCH_3$
5. 4,4´-bis((4-anilino-6-(N-methyl-N-2-hydroxyethyl)amino-1,3,5-triazin-2-yl)amino)stilbene-2,2´-disulfonic acid		 $-N(CH_3)CH_2CH_2OH$
6. 4,4´-bis((4-(3-sulfoanilino)-6-(2-hydroxyethyl)amino-1,3,5-triazin-2-yl)amino)stilbene-2,2´-disulfonic acid		 $-N(H)CH_2CH_2OH$
7. 4,4´-bis((4-(2,5-disulfoanilino)-6-morpholino-1,3,5-triazin-2-yl)amino)stilbene-2,2´-disulfonic acid		
8. 4,4´-bis((4-anilino-6-bis(2-hydroxyethyl)amino-1,3,5-triazin-2-yl)amino)stilbene-2,2´-disulfonic acid		 $-N(CH_2CH_2OH)_2$
9. 4,4´-bis((4-(2,5-disulfoanilino)-6-bis(ethyl)amino-1,3,5-triazin-2-yl)amino)stilbene-2,2´-disulfonic acid		 $-N(CH_2CH_3)_2$

obtained at some point with each FWA. However, the actual amount of FWA exhausting from each bath was determined by UV/Visible spectroscopy. Before applying the FWA's, a calibration curve was prepared for each FWA dyebath with a range of 0 to 100% exhaustion. After treatment the remaining solution was cooled to room temperature in darkness and the absorbing qualities of the solution at the wavelength of maximum absorbance was determined and converted to percent transmittance. By comparing the percent transmittance to the calibration curve, the exact amount exhausting and, thus, the concentration of FWA on the fabric was determined.

Xenon Light Exposure

All samples were exposed in an Atlas Xenon Arc Fade-Ometer, Model 25-WT according to AATCC Test Method 16E, Colorfastness to Light: Water Cooled Xenon-Arc Lamp, Continuous Light (9). Borosilicate inner and outer filters were used to simulate natural, unfiltered sunlight. Fabrics were backed with white bristol, 100% rag, 2-ply paper as suggested by the test method and exposed to 0, 10, 20, 40, 80, and 160 AATCC Fading Units (AFU's) based on the Blue Wool Lightfastness Standards. These levels were selected from pilot tests in which the greatest fading occurred prior to 20 AFU's of exposure, and fading became nearly constant after 160 AFU's. The black panel thermometer temperature during exposure was 145 ± 5 F, as recommended in the above test method, whereas the relative humidity was maintained at 55 ± 5% because 30 ± 5% could not be obtained in the Fade-Ometer.

Evaluation of the Lightfastness of FWA's

Whiteness and Chromaticity Evaluation

After xenon light exposure, changes in whiteness and color were evaluated instrumentally with a Hunterlab Color Difference Meter, Model D-25 Signal Processor and Optical Head, interfaced with a Tektronix 31 programmable calculator. The CIE tristimulus values (X,Y, and Z) were converted into WI E313 whiteness index and CIE 1976 L*a*b* uniform color solid coordinates. All measurements were made on a single layer thickness of fabric backed with a standard white tile provided with the instrument using a 2 inch diameter aperture opening. Three readings were taken on each sample and averaged prior to calculating any change in whiteness or color.

The whiteness index (WI) was calculated according to ASTM Test Method E313-73, Indexes of Whiteness and Yellowness of Near Opaque Materials (11). Values of WI above 100 in this scale denote a bluish white. Because the magnitude of the change in whiteness (ΔWI) following light exposure, especially after 80 and 160 AFU's, was influenced by the initial increase in whiteness due to the FWA treatments ($\Delta WI'$), percentage change in the initial whiteness after 10, 20, 40, 80, and 160 AFU's of xenon exposure was calculated as shown below:

$$\text{\% Change in Whiteness} = \frac{\Delta WI}{\Delta WI'} \times 100$$

where:

$$\Delta WI = WI_{\substack{\text{exposed}\\\text{FWA-treated}}} - WI_{\substack{\text{unexposed}\\\text{FWA-treated}}}$$

$$\Delta WI' = WI_{\substack{\text{unexposed}\\\text{FWA-treated}}} - WI_{\substack{\text{unexposed}\\\text{untreated control}}}$$

The L*a*b* values correspond to the lightness/darkness, redness/greeness, and blueness/yellowness axes of the three dimensional color solid. Color change, ΔL^*, Δa^*, and Δb^* and total color difference, ΔE, in CIELAB units, were determined prior to and following 10, 20, 40, 80, and 160 AFU's of xenon exposure using the CIE 1976 L*a*b* color difference formula which takes the difference between the L*, a*, and b* values (means) for the untreated unexposed and treated samples, squaring these values, adding them together, and then calculating the square root as shown:

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

where:

$$\Delta L^* = L^*_{\text{FWA-treated}} - L^*_{\substack{\text{unexposed}\\\text{untreated control}}}$$

$$\Delta a^* = a^*_{\text{FWA-treated}} - a^*_{\substack{\text{unexposed}\\\text{untreated control}}}$$

$$\Delta b^* = b^*_{\text{FWA-treated}} - b^*_{\substack{\text{unexposed}\\\text{untreated control}}}$$

Fluorescence Evaluation

When FWA´s are degraded by light, their fluorescent properties usually are decreased. A loss in fluorescence may be attributed to either a reduction in the amount of UV radiation absorbed or to a reduction in the ability of the molecule to convert the UV energy to higher, visible wavelengths. A SPEX Fluorolog spectrofluorometer, Model 1902, was used to measure the relative fluorescent intensity of the FWA treated cotton after 0, 10, 20, 40, 80, and 160 AFU´s of light exposure. Rather than performing standard emission (E) measurements, ratio-emission (E/R) measurements were used. This mode automatically corrects the excitation spectra for variations in the excitation radiation by means of a reference detector equipped with a rhodamine B quantum counter (R). A setting of 100 pulses per second was used. Excitation and emission spectra were collected to determine the wavelengths of maximum excitation and emission for each FWA. Relative fluorescent intensity was then measured at the maximum wavelengths. For all the FWA´s evaluated, the wavelength of maximum excitation was 400 nm with a slit width of 0.5 nm and maximum emission of 450 nm with a slit width of 4.0 nm on the fabric substrates. The fabric was folded to obtain a three layer thickness and placed between Dynasil 4000 fused silica glass (obtained from Mark Optics Inc., 1404 E. Gertrude Place, Santa Ana, CA 92705). The glass plates and fabric were then placed into the solid sample holder. This sandwiching effect gave a smoother fabric surface allowing better repeatability between readings.

The change in relative fluorescence intensity (ΔF) following xenon exposure was influenced by the initial increase in fluorescence due to the FWA treatments ($\Delta F'$), therefore, the percentage change in the initial relative fluorescence intensity was calculated following 10, 20, 40, 80, and 160 AFU's of exposure as shown below:

$$\text{\% Change in Relative Fluorescence Intensity} = \frac{\Delta F}{\Delta F'} \times 100$$

where:

$$\Delta F = F_{\substack{\text{exposed}\\ \text{FWA-treated}}} - F_{\substack{\text{unexposed}\\ \text{FWA-treated}}}$$

$$\Delta F' = F_{\substack{\text{unexposed}\\ \text{FWA-treated}}} - F_{\substack{\text{unexposed}\\ \text{FWA-treated}}}$$

Breaking Strength

Changes in breaking strength (BS) is one of the most widely used methods for assessing the effects of light on fiber properties. Tests were conducted according to ASTM Test Method D1682-64, Breaking Load and Elongation of Textile Fabrics, using the one inch raveled strip method (10). Samples treated with FWA's at concentrations of 0.05 and 1.0% owf, as well as the control, were evaluated in the warp direction of the fabric specimens prior to and following 160 AFU's of light exposure. A Scott CRE Tensile Tester with a 3 inch gage length and 100 pound load cell were used. The crosshead speed was set at 2 cm/min to obtain a 20 ± 3 second time to break on the unexposed untreated sample.

Prior to xenon exposure, percentage change in breaking strength was computed to determine if the FWA treatments appreciably influenced the physical properties of the cotton fabric as shown:

$$\begin{array}{c}\text{\% Change in} \\ \text{Breaking Strength}\end{array} = \frac{BS_{\substack{\text{unexposed} \\ \text{FWA-treated}}} - BS_{\substack{\text{unexposed} \\ \text{untreated control}}}}{BS_{\substack{\text{unexposed} \\ \text{untreated control}}}} \times 100$$

After xenon exposure, the samples were evaluated for percentage change in breaking strength to determine if the FWA´s accelerated phototendering and to evaluate the relationship between the lightfastness of the FWA´s and changes in breaking strength based on the exposed untreated control as shown below:

$$\begin{array}{c}\text{\% Change in} \\ \text{Breaking Strength}\end{array} = \frac{BS_{\substack{\text{exposed} \\ \text{FWA-treated}}} - BS_{\substack{\text{exposed} \\ \text{untreated control}}}}{BS_{\substack{\text{exposed} \\ \text{untreated control}}}} \times 100$$

Statistical Analysis

Statistical analyses were performed on the data obtained from percentage change in whiteness, relative fluorescent intensity, and breaking strength. Analysis of variance procedures were used to determine the extent to which the type and concentration of the FWA influences lightfastness and fiber degradation. Duncan´s Multiple Range Tests were performed on the data if F was significant. The level of confidence used in all statistical tests was 0.05. Data obtained from the chromaticity evaluation was used to explain changes in whiteness and fluorescence which occurred in the cotton fabric due to application of the FWA and following xenon exposure.

RESULTS and DISCUSSION

Fluorescent whitening agents (FWA's) function by absorbing ultraviolet radiation present in sunlight or artificial light and converting it to visible blue light. They frequently are applied to textiles to improve their apparent whiteness by increasing the amount of blue light reflected from a fabric. Hence, fabrics appear whiter because a blue hue, rather than yellow, is perceived and relative brightness is increased.

Because of the higher energy associated with UV radiation, as compared to visible radiation, there is greater potential for fading and fiber degradation to occur when FWA's are applied, compared to dyes. FWA's are similar to dyestuffs in that fading characteristics as well as their ability to accelerate phototendering in fibers are influenced by the light source, environmental or exposure conditions, substrate, and the chemical structure of the FWA, including chemical class and functional (auxochromic) groups present. Numerous studies have evaluated the lightfastness and phototendering characteristics of dyes based on chemical structure, but few have investigated how the chemical structure of FWA's influences fading (i.e., loss of fluorescence) and fiber degradation during light exposure.

Because of the commercial significance of FWA's in the textile industry and the lack of available research on the relationship between their chemical structure and lightfastness properties, this study investigated how selected functional or auxochromic groups on triazinylamino stilbene type FWA's affected loss of fluorescence (fading) during xenon exposure and phototendering in cotton. The triazinylamino stilbene chemical class encompasses a large percentage of FWA´s used on cotton.

Nine FWA´s were chosen for investigation based on chemical structure (i.e., pendent functional groups), commercial importance, and availability. All major producers/distributors of FWA´s in the United States were contacted concerning specific products manufactured or sold by their companies. Even though FWA´s are sold under a variety of tradenames, many of these products have identical chemical structures. At the request of the companies who cooperated with the investigator, specific tradenames are not given for the FWA´s, and they are designated only by chemical name. However, included in the list are the majority of the triazinylamino stilbene type FWA´s which have the greatest commercial significance in the U.S. textile industry for improving the whiteness of cotton textiles. They also are used widely in detergent formulations to replentish fabric whiteness during laundering.

The concentration of FWA applied to cotton-containing fabrics in the textile mill varies, depending on their fluorescence effectiveness (i.e., improvement in whiteness associated with a specific concentration). Because of the different concentrations used commercially and the possible interaction between concentration and lightfastness properties, the nine FWA´s were applied to a 100% cotton fabric at concentration levels of 0.05, 0.50, and 1.0% owf. In total, there were 28 treatments which included 27 FWA applications (9 FWA´s x 3 concentrations) and an untreated control. Two replicas of identically treated samples were prepared to evaluate reproducibility of test results.

Subsequent to the application of the FWA´s, as described previously, individual samples were exposed to 10, 20, 40, 80, and 160 AFU´s of xenon light and evaluated for lightfastness by percentage changes in initial whiteness and relative fluorescence intensity, and color change and total color difference. Because of the size of the study, phototendering of the cotton substrate, measured by percentage changes in breaking strength, were conducted on the untreated and FWA-treated samples at 0.05 and 1.0% owf concentrations after 0 and 160 AFU´s of xenon exposure.

Theoretical Versus Actual Concentration of FWA on the Fabric

Due to differences in chemical structure of the FWA´s, the actual concentration (amount of FWA present on the fabric) differed from the theoretical concentration (amount of FWA initially present in the dyebath). Theoretically, dyebaths were prepared at 0.05, 0.50 and 1.0% owf. However, the percentage of the FWA that actually exhausted from the dyebath was not 100%, and differed with each FWA as shown in Table 3.

The theoretical concentration was most similar to the actual concentration at the 0.05% owf level, with the actual concentration ranging from 0.02 to 0.05% owf. At higher theoretical concentrations (i.e., 0.50 and 1.0% owf), the range for the actual concentration on the fabric was much wider. At the 0.50% owf theoretical concentration, the actual concentration ranged from 0.07 to 0.42% owf; and at the 1.0% owf theoretical concentration, the actual

Table 3. Actual Percentage of FWA´s Present on the Cotton Fabric at each Theoretical Concentration

FWA	Theoretical Concentration (% owf)	Actual Concentration, % owf		
		replica		
		1	2	Mean
1	0.05	0.04	0.04	0.04
	0.50	0.21	0.21	0.21
	1.0	0.27	0.29	0.28
2	0.05	0.04	0.04	0.04
	0.50	0.23	0.24	0.24
	1.0	0.32	0.31	0.32
3	0.05	0.04	0.04	0.04
	0.50	0.22	0.22	0.22
	1.0	0.31	0.30	0.30
4	0.05	0.04	0.04	0.04
	0.50	0.15	0.17	0.16
	1.0	0.21	0.21	0.21
5	0.05	0.05	0.05	0.05
	0.50	0.41	0.42	0.42
	1.0	0.65	0.67	0.66
6	0.05	0.03	0.03	0.03
	0.50	0.11	0.11	0.11
	1.0	0.14	0.13	0.14
7	0.05	0.02	0.02	0.02
	0.50	0.06	0.09	0.07
	1.0	0.07	0.10	0.08
8	0.05	0.05	0.05	0.05
	0.50	0.38	0.39	0.38
	1.0	0.56	0.58	0.57
9	0.05	0.02	0.02	0.02
	0.50	0.07	0.08	0.08
	1.0	0.09	0.09	0.09

concentration ranged from 0.08 to 0.66% owf. Past researchers investigating the lightfastness and phototendering of fibers due to FWA's have only reported the theoretical concentrations applied. Interpretation of results based on these values would be very easy but may not necessarily be accurate.

Extensive pilot tests were conducted to determine if each FWA could be applied at the same actual concentration on the fabric. By changing the theoretical concentration of each individual dyebath, it was assumed that at some point the actual concentration on the fabric would be the same for each FWA. However, when altering the concentration of the dyebath to exhaust greater or lesser amounts of FWA onto the fabric, it was found that the relationship between concentration of the bath and amount exhausting differed for each FWA. Therefore, preparing suitable baths at three concentrations for 9 FWA's to exhaust the same amount on the fabric was economically unfeasible in terms of time, fabric, and chemicals because it became a trial and error task. With some FWA's this also produced undesirable results. When the concentration of one FWA was raised to an average level for all the FWA's the inherent yellow color of that FWA became obvious. When the concentration of other FWA's was decreased to this same level, there was no whitening effect due to the low concentration present. Because the investigator also wanted to maintain the concentration at a level similar to that used industrially and that would give a maximum whitening effect, applying the same amount of each FWA to the fabric was not possible.

All percentages referring to concentration in this study are based on the active chemical ingredient of FWA, rather than on percent of a commercial product or emulsion system. Researchers in the past have based their work on commercial products of which there is no indication of the concentration of the active ingredient in the formulated product. Hence, many of the concentrations of FWA´s used in previous studies were based on the percent of total commercial product and not on the actual amount (% owf) of FWA present. The results obtained when basing the research on percent of a commercial product versus percent of FWA may not agree.

Visual Assessment of Whiteness and Chromaticity

No attempt was made in this study to visually evaluate the whiteness or chromaticity of the fabrics. However, it is important to point out obvious visual differences, especially among concentrations or xenon exposure levels which will assist in the explanation of test results. Since the light source used when viewing the samples can influence preceivable differences due to the amount of ultraviolet radiation present, the samples were all viewed using a McBeth Lab Lite under north sky daylight.

Effect of FWA´s on Fabric Whiteness, Fluorescence Intensity, and Chromaticity

The effects of the nine FWA´s, applied at three concentrations (0.05, 0.50, and 1.0% owf), on the appearance of the untreated cotton fabric were determined by evaluating changes in whiteness, relative fluorescence intensity, and chromaticity.

Whiteness

The mean whiteness index (WI) and changes in whiteness index values initially ($\Delta WI'$) for the untreated and FWA-treated samples prior to xenon exposure are presented in Table 4. Replication means for the whiteness index (WI) and change in whiteness index ($\Delta WI'$) values are shown in Tables A1 and A2 of Appendix A, respectively. The change in whiteness index initially was calculated as shown:

$$\Delta WI' = WI_{\text{FWA-treated}} - WI_{\text{untreated control}}$$

The mean WI value for the unexposed untreated cotton fabric, based on two replicas (each containing three measurements), was 81.2 which is typical for bleached 100% cotton. In general, all of the FWA treatments increased the apparent whiteness of the cotton fabric. The whiteness index values of the FWA-treated cotton ranged from 100.8 (FWA 9, 0.05% owf) to 125.5 (FWA 1, 1.0% owf) with a value greater than 100 corresponding to a blue white. The corresponding changes in whiteness index values ($\Delta WI'$), which ranged from 19.4 to 44.2, demonstrated the relative increases in whiteness that can occur when FWA's are applied to cotton.

Also of interest in this study was the relationship between chemical structure of the FWA's, the actual amounts that exhausted onto the fabric, and the resulting changes in whiteness. At the theoretical concentration of 0.05% owf, the actual concentrations for the FWA's ranged from 0.02 to 0.05% owf. FWA's 5 and 8 had the

Table 4. Influence of FWA Treatments on the Whiteness Properties of 100% Cotton Fabric

FWA	Concentration (% owf)	Whiteness	
		WI	ΔWI´
Control	0.0	81.2	——
1	0.05	109.1	27.8
	0.50	125.0	43.8
	1.0	125.5	44.2
2	0.05	106.4	25.0
	0.50	122.8	41.5
	1.0	123.8	42.6
3	0.05	112.8	31.4
	0.50	122.4	41.0
	1.0	120.8	39.6
4	0.05	124.1	42.8
	0.50	118.7	36.4
	1.0	113.4	32.2
5	0.05	114.2	33.0
	0.50	125.3	44.0
	1.0	122.2	41.0
6	0.05	113.6	32.2
	0.50	124.8	43.4
	1.0	124.6	43.3
7	0.05	108.4	26.2
	0.50	123.4	42.0
	1.0	125.2	43.9
8	0.05	117.2	35.8
	0.50	122.6	41.3
	1.0	116.2	34.9
9	0.05	100.8	19.4
	0.50	116.8	35.4
	1.0	120.4	39.2

exhaustion with actual concentrations of 0.05%. Both of these FWA's had an anilino group in the X position (without sulfonic acid water solubilizing groups), and either a mono- (FWA 5) or di-hydroxyethyl (FWA 8) amino group in the Y position on the triazinylamino stilbene parent structure.

FWA's 1, 2, 3, and 4 had actual concentrations of 0.04% owf. Among these FWA's, 3 and 4 also had an anilino group (without sulfonic acid groups) in the X position. However, the functional groups in the Y position were different from those in FWA's 5 and 8. FWA 3 contained an hydroxy propoxy group and FWA 4 contained a methoxy group in the Y position. In both of these FWA's, the Y group contained an oxygen linkage which connected it to the parent structure, whereas FWA's 5 and 8 had an amino group. Hence, FWA's 3, 4, 5, and 8 differed only in the Y functional group, with the amino Y groups exhibiting slightly higher exhaustion than the FWA's that had methoxy or propoxy Y functional groups. FWA's 1 and 2 also exhibited actual concentrations of 0.04%. They differed from FWA's 3, 4, 5, and 8 in that they both had a sulfoanilino group in the X position, but were similar to FWA 8 in that they both contained a dihydroxyethyl amino group in the Y position. FWA 6 was similar in chemical structure to FWA's 1 and 2, but it only had one hydroxyethyl group on the amino moiety in the Y position. The actual concentration of FWA 6 was 0.03% owf; hence, the more polar dihydroxyethyl amino group in the Y positions may have facilitated exhaustion.

The lowest actual concentrations of 0.02% owf were obtained from FWA's 7 and 9 which had two sulfonic acid groups on the anilino group in the X position and either a diethyl amino (FWA 9) or a morpholino (FWA 7) group in the Y position which are both relatively nonpolar, compared to the hydroxy compounds and would have less affinity for cotton. Thus, the X and Y functional groups appeared to influence the percentage of the FWA that exhausted onto the fabric. As in direct dye chemistry, an increase in the number of sulfonic acid groups on the parent FWA molecule creates a more negative compound which has less affinity for the cotton fiber. In this study, as the number of water solubilizing sulfonic acid groups on the anilino group increased, exhaustion decreased. The polarity of the functional groups in the Y position also influenced exhaustion. Those FWA's that had dihydroxy amino groups in the Y position exhibited somewhat greater exhaustion than did those containing monohydroxyethyl amino or morpholino groups.

Similar differences were observed in the exhaustion characteristics of the FWA's at the theoretical concentrations of 0.50% and 1.0% owf. FWA's 5 and 8 exhibited the greatest exhaustion, whereas FWA's 6, 9, and 7 had the lowest actual concentrations which served as a verification of the findings at the 0.05% concentration level. At the 0.50% and 1.0% owf treatments, there was a greater range in the actual concentrations for FWA's 1, 2, 3, and 4, whereas in the lowest concentration level their actual concentrations were 0.04% owf. The greater ranges of values at the higher concentrations facilitated better discrimination among these FWA's, and their rank order of actual concentration at both the 0.50 and 1.0% theoretical applications was 2, 3, 1, and 4, with 4 having considerably lower

FWA´s 2, 3, and 1 had almost identical actual concentrations at both the 0.50% (0.24%, 0.22%, and 0.21%, respectively) and 1.0% owf levels (0.32%, 0.30%, and 0.28% owf, respectively). FWA 4 did not contain hydroxy groups on the Y moiety which probably accounts for its slightly lower exhaustion.

The FWA that produced the greatest increase in whiteness at the 0.05% theoretical concentration was FWA 4 (WI = 124.1), followed by FWA´s 8, 5, 6, 3, 1, 7, 2, and 9 (WI = 100.8). However, the increases in whiteness associated with the nine FWA´s must be discussed relative to the actual concentration present because the FWA´s differed in exhaustion properties. In general, as the amount of FWA increased, whiteness values increased up to the point where the FWA would self-extinguish and fluorescence and whiteness decreased. The concentration which produced the greatest increase in whiteness differed among the FWA´s.

At the 0.05% theoretical concentration, FWA´s 5 and 8 had the highest actual concentration (0.05%) and the highest whiteness values (114.2 and 117.2), except for FWA 4, which had an appreciably greater increase in whiteness (124.1). FWA 4 contained an anilino group in the X position and a methoxy groups in the Y position which are both electron donating groups. Previous research has shown that electron donating groups (i.e., $-NH_2$, $-NHR$, $-OH$, and $-OCH_3$) increase fluorescence intensity (22,42,91). In addition to providing greater whiteness than the FWA´s that had equivalent (FWA´s 1, 2, and 3) or greater concentrations (FWA´s 5 and 8), lower WI values were obtained at higher concentrations for FWA 4 which further illustrated its fluorescence effectiveness at low concentrations (i.e., at 0.04% owf it was near the point of optimum concentration for maximum fluorescence).

Among the other FWA´s that also had actual concentrations of 0.04% owf at the 0.05% owf theoretical concentration, (FWA´s 1, 2, and 3), those containing a sulfoanilino group in the X position on the parent structure (FWA´s 1 and 2) had lower whiteness values than those containing only an anilino group without sulfonic acid groups (FWA´s 4 and 3). Hence, the sulfonic acid groups, which are electron withdrawing, appeared to reduce exhaustion and fluorescence. FWA´s 1 and 2 had identical chemical structures except for the location of the sulfonic acid group on the anilino group. A slightly higher WI value (109.1) was obtained for FWA 1 with the sulfonic acid group in the meta position, compared to FWA 2 (106.4) with the sulfonic acid group in the para position. Previous research has shown that electron withdrawing and electron donating groups on a benzene ring in the para position decreases fluorescence (91) and may decrease it more than one in a meta position.

FWA´s 7 and 9 had the lowest actual concentration (0.02% owf), which was attributed to the disulfoanilino group in the X position, but differed in whiteness index values. The whiteness value (108.4) of FWA 7 was greater than that obtained for FWA 9 (100.8), but was similar to those obtained for FWA´s with higher concentrations (FWA 2 and 1). This may be attributed to the morpholino group in the Y position which contains easily excited, nonbonded electrons on the N and O atoms which facilitate resonance and possibly the absorption of

UV radiation or its subsequent conversion to visible wavelengths.

As mentioned previously, the higher concentrations (i.e., 0.50 and 1.0% owf) of the FWA's did not always produce greater whiteness (see Table 4). This is due to the inherent yellow color of the FWA becoming apparent at higher concentrations, resulting in a lower whiteness index value. The concentration at which the yellow color became obvious on the fabric was different for each FWA, depending on its chemical structure and fluorescent properties.

Except for FWA 4 which had the highest $\Delta WI'$ at the 0.05% owf concentration, all of the FWA's increased the whiteness of the cotton when applied at a theoretical concentration of 0.50% owf. However, the actual concentrations of the FWA's at the 0.50% owf level ranged from 0.07 to 0.42%. The highest application levels (0.21% owf to 0.42% owf) were obtained from FWA's 1, 3, 2, 8, and 5 (highest). Even though the range of the concentrations was considerably large, they had similar whiteness values (122.4 to 125.3) which may reflect the maximum increase in whiteness that can be obtained with FWA's before they begin to self-extinguish. Because there is a maximum concentration level beyond which whiteness no longer increases, it is difficult to correlate concentration, FWA type, and resulting increases in whiteness. However, those FWA's that had the lowest WI values at the 0.05% owf concentration, also exhibited the greatest increase in whiteness at the 0.50% owf concentration. FWA's 6 and 7 had considerably lower actual concentrations than those discussed above (0.11% and 0.07% owf), but comparable WI values which supported the findings reported for the lower concentration (i.e., they had very good fluorescence properties), whereas FWA 9 was considerably less effective (WI = 116.8), compared to FWA´s 6 and 7 which had similar concentrations. It also had the lowest WI values at the 0.50% owf concentration level.

A further decrease in whiteness occurred in FWA 4 when applied at 1.0% owf. FWA 4 was the only FWA to experience a decrease in whiteness at both the 0.50% and 1.0% concentration levels. The actual amount of FWA on the fabric was moderate, as compared to the other FWA´s, and yet due to the properties of the FWA the whitening effect was self-extinguished even at the 0.50% owf concentration. FWA 8 and 5, which had the second and third highest WI values at the 0.05% owf concentration also exhibited an appreciable decrease in whiteness at 1.0% owf, compared to the values obtained at 0.50% owf, as did FWA 3 except the decrease was considerably less. Thus, FWA´s 3, 5, and 8 exhibited maximum fluorescence at the 0.50% owf concentration, showing a decrease in whiteness at the 1.0% owf level.

Only FWA 9, which had the lowest WI value when applied at 0.05 and 0.50% owf, exhibited an appreciable increase in whiteness at the highest concentration of 1.0% owf. FWA´s 2 and 7 exhibited only a slight increase in whiteness at the 1.0% owf concentration. Hence, FWA´s 2, 7, and 9 were not applied at a concentration high enough to self-extinguish the fluorescence and they may not have reached the highest whiteness achievable. On the other hand, no appreciable changes were observed in the WI values for FWA 1 and 6 when applied at 1.0% owf, compared to 0.50% owf. Hence, there was no consistent pattern between the amount of FWA on the fabric and the amount of whitening that occurred. Each FWA has its own specific properties in terms of fluorescence effectiveness and optimum concentration level.

Relative Fluorescence Intensity

The mean relative fluorescence intensity values (F) and change in relative fluorescence intensity initially ($\Delta F'$) for the untreated and FWA-treated samples prior to xenon exposure are given in Table 5 with replica means for relative fluorescence intensity in Table A3 and change in relative fluorescence intensity initially in Table A4, Appendix A. Change in relative fluorescence intensity initially was calculated as shown:

$$\Delta F' = F_{\text{FWA-treated}} - F_{\text{untreated control}}$$

As was expected, the untreated cotton had little or no inherent fluorescence which was reflected in the fluorescence intensity value of 0.02, whereas the values for the FWA-treated samples ranged from 0.72 (FWA 9, 0.05% owf) to 1.10 (FWA 7, 1.0% owf). The fluorescence intensity values at the 0.05% owf concentration paralleled the whiteness index values (both WI and $\Delta WI'$) very closely for each FWA, with an increase or decrease in whiteness being accompanied by an increase or decrease in fluorescence intensity. However, at the 0.50 and 1.0% owf concentrations, the highest whiteness value did not always correspond to the highest fluorescence intensity value which was probably due to differences in fluorescence effectiveness of the

Table 5. Influence of FWA Treatments on the Fluorescence Properties of 100% Cotton Fabric

FWA	Concentration (% owf)	Relative Fluorescence Intensity	
		F	ΔF
Control	0.0	0.02	----
1	0.05	0.80	0.78
	0.50	1.04	1.02
	1.0	1.03	1.00
2	0.05	0.79	0.76
	0.50	1.00	0.98
	1.0	1.01	0.98
3	0.05	0.86	0.83
	0.50	0.97	0.94
	1.0	0.94	0.92
4	0.05	1.00	0.98
	0.50	0.92	0.90
	1.0	0.84	0.82
5	0.05	0.91	0.88
	0.50	1.05	1.02
	1.0	1.04	1.00
6	0.05	0.90	0.88
	0.50	1.06	1.04
	1.0	1.03	1.00
7	0.05	0.84	0.82
	0.50	1.08	1.04
	1.0	1.10	1.08
8	0.05	0.98	0.95
	0.50	1.04	1.01
	1.0	0.95	0.92
9	0.05	0.72	0.69
	0.50	0.97	0.94
	1.0	1.02	1.00

FWA's and the effects of applying more than the optimum concentration.

Although fluorescence intensity may be expected to increase as concentration of the FWA present is increased, there is a limited concentration range within which the effectiveness of FWA's are maximized. Self-extinguishment can occur whether or not the fabric yellows when excessive concentrations of the FWA are applied (beyond that which is required to obtain desirable whiteness). Increases in the fluorescence intensity (due to increases in concentration not accompanied by yellowing) may not be recorded if all available UV radiation from the incident light source has already been absorbed. In this case, for an increase in fluorescence intensity to be recorded it would be necessary to increase the amount of UV radiation in the incident light source. In other words, the FWA has absorbed all the UV radiation available to it, converting it to visible blue light, and would need additional UV radiation to excite it any further. However, when excessive concentrations of FWA's are applied it is generally accompanied by an increase in yellowness due to the inherent yellow color of the FWA. Any increases in fluorescence intensity which might have occurred may not be recorded because the additional blue fluorescent light emitted by the FWA is re-absorbed by the yellow color on the textile.

Chromaticity

L*a*b*, color change (ΔL*, Δa*, and Δb*), and total color difference values (ΔE) were recorded for the untreated and FWA-treated cotton to obtain a better understanding of how the FWA's influenced chromaticity as shown in Table 6. Color change and total color difference were calculated as shown:

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

where:

$$\Delta L^* = L^*_{\text{FWA-treated}} - L^*_{\text{untreated control}}$$

$$\Delta a^* = a^*_{\text{FWA-treated}} - a^*_{\text{untreated control}}$$

$$\Delta b^* = b^*_{\text{FWA-treated}} - b^*_{\text{untreated control}}$$

The L* value can range from 0 to 100 corresponding to maximum darkness and maximum lightness, respectively. The a* and b* values can be positive or negative, corresponding to redness (+a) or greeness (-a) and yellowness (+b) or blueness (-b), respectively. Color difference is a measure of the total amount of color change that has occurred in the fabric, with only positive values obtainable, thus it does not reflect the type of hue shifts or color changes that have actually taken place.

In this study, the color difference values associated with the steps (or pairs of gray chips representing increasing amount of color difference) on the AATCC Gray Scale for Color Change were used as a reference for assessing colorimeteric data for FWA-treatments and xenon exposures (9). AATCC specifies a step 5, negligible or no change, on the Gray Scale for Color Change, as 0 ± 0.2 CIELAB units of color difference; step 4, slightly changed, as 1.7 ± 0.3 CIELAB units; step 3, noticeably changed, as 3.4 ± 0.4 CIELAB units; step 2, considerably changed, as 6.8 ± 0.6 CIELAB units; and step 1, much

Table 6. Influence of FWA Treatments on the Chromaticity of 100% Cotton Fabric

FWA	Concentration (% owf)	Chromaticity						
		L*	a*	b*	ΔL*	Δa*	Δb*	ΔE
Control	0.0	94.8	-0.7	1.1	---	---	---	---
1	0.05	95.0	1.8	-3.8	0.1	2.5	-4.9	5.5
	0.50	95.2	3.4	-6.5	0.3	4.1	-7.6	8.6
	1.0	95.2	3.5	-6.6	0.3	4.2	-7.6	8.8
2	0.05	95.0	1.4	-3.3	0.2	2.1	-4.4	4.9
	0.50	95.0	3.2	-6.2	0.2	3.8	-7.2	8.2
	1.0	95.2	3.2	-6.3	0.3	4.0	-7.4	8.4
3	0.05	95.0	2.0	-4.4	0.1	2.8	-5.6	6.2
	0.50	95.0	3.1	-6.0	0.2	3.9	-7.2	8.2
	1.0	95.2	3.0	-5.8	0.4	3.7	-6.8	7.5
4	0.05	95.0	3.2	-6.4	0.2	3.9	-7.4	8.4
	0.50	95.1	2.8	-5.4	0.2	3.6	-6.5	7.4
	1.0	95.2	2.4	-4.5	0.3	3.1	-5.6	5.4
5	0.05	95.0	2.2	-4.7	0.2	2.9	-5.8	5.6
	0.50	95.0	3.6	-6.6	0.2	4.3	-7.6	8.8
	1.0	95.2	3.2	-6.0	0.4	4.0	-7.0	8.1
6	0.05	95.0	2.1	-4.6	0.2	2.8	-5.6	6.4
	0.50	95.1	3.3	-6.4	0.3	4.0	-7.6	8.6
	1.0	95.1	3.3	-6.4	0.3	4.0	-7.5	8.6
7	0.05	95.0	1.6	-3.7	0.1	2.4	-4.8	5.4
	0.50	95.0	3.2	-6.2	0.2	3.8	-7.4	8.3
	1.0	95.1	3.4	-6.6	0.3	4.1	-7.6	8.6
8	0.05	95.0	2.4	-5.2	0.2	3.2	-6.3	7.0
	0.50	95.2	3.2	-6.0	0.3	4.0	-7.2	8.2
	1.0	95.2	2.6	-5.0	0.4	3.4	-6.0	6.9
9	0.05	94.9	0.9	-2.4	0.1	1.6	-3.5	3.8
	0.50	95.0	2.4	-5.1	0.2	3.2	-6.2	7.0
	1.0	95.0	2.8	-5.8	0.2	3.5	-6.8	7.7

changed as 13.6 ± 1.0 CIELAB units.

The mean CIE 1976 L*a*b* values for the unexposed untreated cotton were L* = 94.8, a* = -0.7, and b* = -1.1, indicating that even though the untreated cotton fabric was considered white it had a slightly yellow hue.

In general, the color difference values (ΔE) correspond closely to changes in whiteness index values (ΔWI´), with an increase or decrease in whiteness for each FWA accompanied by an increase or decrease in color difference. Because ΔE values only indicate total color difference, ΔL*, Δa*, and Δb* values were used to assess the type of color change that occurred in the samples.

All of the FWA´s increased the whiteness of the cotton with ΔE values ranging from 3.8 to 8.8 which would correspond to "noticeably changed" and "considerably changed", respectively. Little or no appreciable change in the L* values occurred in the FWA-treated samples, compared to the untreated control (L* = 94.8), with ΔL* values ranging from 0.1 to 0.4 units. The majority of the color difference was attributed to changes in the a* and b* values.

All of the a* values became positive, denoting a red color, when the FWA´s were applied to the cotton. The color change (from slightly green on the untreated cotton to the slight red of the treated cotton) suggests that the emitted fluorescent light contained some red wavelengths. The a* values for the FWA treated fabric ranged from 0.9 (FWA 9, 0.05% owf) to 3.6 (FWA 5, 0.50% owf), which corresponded to Δa* values of 1.6 to 4.3 units, respectively. Generally, for each FWA, changes in the the a* value paralleled the whiteness index value very closely with an increase or decrease in redness being accompanied by an increase or decrease in whiteness for each FWA.

The FWA treatment on the cotton fabric caused the largest shift in the b* value from yellow (+b*) to blue (-b*), with values ranging from -2.4 (FWA 9, 0.05% owf) to -6.6 (FWA 5, 0.50% owf) or Δb* values of 3.5 to 7.7 units. In general, the Δb* values were approximately twice as large as the Δa* values, indicating that the FWA's had the greatest effect on blueness, compared to lightness or redness/greeness. The fabric became bluer due to the emitted fluorescent light in the blue region of the visible spectrum. However, the shift of the a* value to red suggests that the color emitted is a violet or reddish blue fluorescence. Again, the b* value followed the whiteness index value with a change in whiteness being paralleled by a change in the b* value for each FWA. The WI values were correlated with the Δa* and Δb* values as expected since the former is based on the a* and b* values.

In summary, the application of the nine FWA's at three concentrations to the 100% cotton fabric increased the whiteness appreciably as noted in the change in whiteness, fluorescence, and chromaticity values. The untreated cotton had a whiteness index value of 81.2 whereas the WI values for the FWA treated samples ranged from 100.8 to 125.5. The chromaticity values were highly correlated with the whiteness values, with the b* value (corresponding to blueness/yellowness) exhibiting the greatest change. The cotton fabric had little or no fluorescence initially with a value of 0.02. The FWA-treated samples had considerably more fluorescence with values ranging from 0.72 to 1.10. At the lowest concentration (0.05% owf) the fluorescence intensity and whiteness index values paralleled one another very closely with an increase or decrease in fluorescence being accompanied by an increase or decrease in whiteness. At higher concentrations the values did not always correspond due to self-extinguishment of the emitted fluorescence and differences in actual concentration of FWA's on the fabric.

The actual concentration of FWA on the fabric at any theoretical concentration was not representative of the whiteness or fluorescence intensity imparted by the FWA. The chemical structure of the FWA's influenced the fluorescence intensity and whiteness. Electron donating groups tended to increase the fluorescence intensity and whiteness, while electron withdrawing groups decreased these values. The amount of FWA exhausting onto the fabric also was influenced by the chemical structure of the FWA. Generally, as the number of sulfonic acid groups increased, the amount of FWA exhausting decreased. The sulfonic acid groups serve as water solubilizing groups but decrease the affinity of the FWA for the cotton. Of the FWA's without any sulfonic acid groups on the anilino group in the X position, those that contained an oxygen as the link between the Y functional group and the parent molecule had lower exhaustion, compared to those containing an amino group as the link. Those with the amino link had hydroxyl end groups which increase the attraction between the FWA molecule and the cotton, also aiding exhaustion.

Effect of Xenon Exposure on the Whiteness, Fluorescence Intensity, and Chromaticity of Untreated and FWA-treated Cotton Fabric

Changes in Whiteness

The whiteness index values (WI) for the nine FWA's applied to 100% cotton at concentrations of 0.05, 0.50, and 1.0% owf and the untreated controls after 10, 20, 40, 80, and 160 AFU's of xenon exposure for each replica of the experiment are presented in Table A1, Appendix A. Each replica mean was based on three readings per specimen. The change in whiteness index (ΔWI) was calculated, based on the whiteness index values of the FWA-treated samples before and after xenon exposure ($\Delta WI = WI_{exposed} - WI_{unexposed}$). The change in whiteness index for each replica of the experiment are given in Table A5, Appendix A. The ΔWI grand means for change in whiteness, which were computed on the replica means, are presented in Table 7. Losses and gains in whiteness are indicated by negative (-) and positive ΔWI values, respectively. The mean ΔWI values for the 27 treatments (9 FWA's x 3 concentrations) and untreated controls, each at five xenon exposure levels, ranged from 0.2 (untreated controls at 160 AFU's) to -55.0 (FWA 5, 0.50% owf at 80 AFU's).

Compared to the unexposed untreated control samples, the untreated cotton had only slightly higher ΔWI values after each subsequent xenon exposure, indicating minimal increases in whiteness. Although a portion of this increase could be attributed to variation in fabric and instruments, there did appear to be a perceivable increase in whiteness at the lowest exposures (i.e., 0.3 ΔWI at 10 AFU's and 0.6 ΔWI at 20 and 40 AFU's). The slight increase in whiteness after 10 and 20 AFU's may have been attributed to the

Table 7. Mean Change in Whiteness Index (ΔWI) at Each Xenon Exposure Level

FWA	Concentration (% owf)	Change in Whiteness Index, ΔWI				
		Exposure (AFU's)				
		10	20	40	80	160
Control	0.0	0.3	0.6	0.6	0.3	0.2
1	0.05	-10.9	-15.3	-20.2	-23.8	-27.0
	0.50	-15.8	-22.8	-29.4	-40.4	-43.4
	1.0	-16.0	-22.8	-29.0	-37.1	-42.2
2	0.05	-10.8	-14.6	-18.8	-22.1	-24.6
	0.50	-14.6	-21.0	-29.4	-39.8	-41.4
	1.0	-15.5	-21.6	-29.4	-36.6	-41.4
3	0.05	-11.5	-16.3	-20.9	-25.4	-28.6
	0.50	-15.3	-22.8	-30.6	-44.0	-43.9
	1.0	-16.9	-24.6	-31.4	-38.6	-43.2
4	0.05	-14.2	-21.1	-27.8	-34.7	-39.2
	0.50	-17.0	-25.4	-35.2	-49.6	-52.2
	1.0	-16.2	-23.8	-32.2	-41.0	-49.6
5	0.05	-13.0	-17.5	-22.6	-28.0	-30.8
	0.50	-20.4	-30.4	-38.4	-55.0	-53.5
	1.0	-21.1	-30.9	-41.6	-51.5	-54.4
6	0.05	-13.2	-18.4	-23.6	-28.8	-31.6
	0.50	-15.5	-23.2	-31.4	-45.5	-44.1
	1.0	-15.7	-23.1	-31.3	-38.9	-43.8
7	0.05	-14.1	-18.6	-22.7	-25.9	-28.0
	0.50	-17.6	-24.6	-31.8	-42.6	-43.1
	1.0	-18.4	-25.6	-32.6	-38.8	-43.8
8	0.05	-13.0	-18.5	-24.0	-28.8	-33.2
	0.50	-19.4	-28.4	-37.4	-50.8	-54.0
	1.0	-20.6	-29.8	-38.8	-47.1	-50.4
9	0.05	-12.2	-15.5	-17.9	-19.5	-20.7
	0.50	-18.1	-24.2	-30.5	-37.1	-37.3
	1.0	-18.8	-26.1	-33.0	-38.0	-41.3

"bleaching effects" of xenon light. As reported earlier, grassing or light bleaching was used historically to whiten textiles prior to the development of chemical bleaches in the early 1800's.

Compared to the WI values for the untreated control at 10 and 20 AFU's of xenon exposure, no additional increase in whiteness was observed in the untreated controls after 40 AFU's, and the ΔWI values decreased slightly after 80 and 160 AFU's. These results were not unexpected since short periods of light exposure may cause photochemical bleaching, whereas prolonged periods of light exposure may cause yellowing in undyed textiles which would result in a decrease in whiteness.

In general, the whiteness of the FWA-treated cotton progressively decreased with increasing xenon exposure as indicated by the magnitude of the - ΔWI values (see Table 7). As FWA's fade on textile substrates, there is a loss in fluorescence and thus, a decrease in fabric whiteness. The amount of fading or the decrease in whiteness in the FWA-treated samples at each xenon exposure level was influenced by many factors. However, preliminary examination of the data indicated that the change in whiteness after each exposure period was greatly influenced by the initial increase in whiteness ($\Delta WI'$) due to the application of the FWA. These values ranged from 19.4 to 44.0 WI units (see Table 4). Hence, the percentage change in the initial whiteness (after FWA treatment) at each xenon exposure level was calculated as follows:

$$\begin{array}{l}\text{\% Change in} \\ \text{Whiteness}\end{array} = \frac{\Delta WI}{\Delta WI'} \times 100$$

where:

$$\Delta WI = WI_{\substack{\text{exposed} \\ \text{FWA-treated}}} - WI_{\substack{\text{unexposed} \\ \text{FWA-treated}}}$$

$$\Delta WI' = WI_{\substack{\text{unexposed} \\ \text{FWA-treated}}} - WI_{\substack{\text{unexposed} \\ \text{untreated control}}}$$

The percentage change in whiteness for the 27 FWA treatments after 10, 20, 40, 80, and 160 AFU's of xenon exposure are presented in Table 8 (replica means are given in Table A6, Appendix A). A negative (-) value indicates a loss in whiteness which was exhibited for all the FWA treatments and exposures, whereas a positive value would indicate an increase in whiteness. The percentage change in whiteness ranged from -33.2% (FWA 4, 0.05% at 10 AFU's) to -155.8% (FWA 4, 1.0% at 160 AFU's). A change in whiteness greater than the amount that was initially gained by the application of the FWA (greater than 100%) suggests that other things were occurring on the fabric and influencing the values. This may include yellowing of the fabric, the point at which self-extinguishment of the fluorescence occurs, and the fluorescence effectiveness which are influenced by FWA type, concentration on the fabric, and xenon exposure level. The interactions among all these variables are quite complex. For example, FWA type influenced which theoretical concentration produced the greatest change in whiteness within the five exposure levels. At the 0.05% concentration FWA's 1, 2, 6, 7, and 9 exhibited the greatest percentage change in whiteness at 10, 20, and 40 AFU's, whereas the

Table 8. Mean Percentage Change in Whiteness at Each Xenon Exposure Level

FWA	Concentration (% owf)	Change in Whiteness, % Exposure (AFU's) 10	20	40	80	160
1	0.05	-39.2	-55.0	-72.9	-85.8	-96.7
	0.50	-36.2	-52.0	-67.2	-92.4	-99.0
	1.0	-36.0	-51.6	-65.6	-83.8	-95.4
2	0.05	-43.0	-58.2	-75.0	-88.3	-98.0
	0.50	-35.0	-50.5	-71.0	-95.4	-99.1
	1.0	-36.4	-50.6	-69.0	-85.8	-97.1
3	0.05	-36.7	-52.0	-66.4	-80.9	-90.6
	0.50	-37.3	-55.6	-74.4	-107.4	-107.0
	1.0	-42.7	-62.2	-79.3	-97.5	-109.0
4	0.05	-33.2	-49.4	-64.8	-81.0	-91.4
	0.50	-45.6	-68.4	-94.4	-133.8	-140.7
	1.0	-51.3	-74.9	-101.0	-128.2	-155.8
5	0.05	-39.4	-53.2	-68.8	-85.2	-93.3
	0.50	-46.5	-69.1	-87.4	-125.1	-121.7
	1.0	-51.7	-75.7	-101.7	-125.6	-133.1
6	0.05	-41.2	-56.9	-73.2	-89.2	-98.1
	0.50	-35.6	-53.4	-72.4	-104.4	-101.2
	1.0	-36.3	-53.4	-72.2	-89.8	-101.0
7	0.05	-52.0	-68.2	-83.6	-95.6	-103.0
	0.50	-41.8	-58.4	-75.4	-101.2	-102.4
	1.0	-41.8	-58.2	-74.1	-88.4	-99.8
8	0.05	-36.4	-51.6	-67.0	-80.4	-92.4
	0.50	-47.0	-69.0	-90.6	-123.3	-131.2
	1.0	-59.6	-86.2	-111.8	-134.9	-145.1
9	0.05	-63.2	-79.6	-92.0	-100.2	-106.1
	0.50	-51.0	-68.4	-86.0	-104.7	-105.2
	1.0	-48.2	-66.6	-84.3	-97.2	-105.4

1.0% concentration resulted in the greatest change in whiteness at these exposures for FWA´s 4, 5, and 8. At higher xenon exposures (i.e., 80 and 160 AFU´s), the concentration level that produced the greatest loss in whiteness differed for the nine FWA types.

The actual concentrations at the 0.50 and 1.0% owf concentration levels often exceeded that required for maximum fluorescence effectiveness, resulting in fluorescence self-extinguishment. This greatly influenced the Δ WI and Δ WI´ values and percentage change in whiteness at these higher FWA concentrations. Thus, it was felt that a better comparison of the fading characteristics of the FWA´s could be obtained from the data for the 0.05% owf theoretical concentration. Hence, a seperate statistical analysis was carried out on the lowest FWA concentration and data interpretation will focus on the results for this level.

Analysis of variance (ANOVA) procedures were used to evaluate the dependence of percentage change in whiteness of the FWA-treated samples on the independent variables: FWA (1-9), concentration (0.05, 0.50, and 1.0% owf), and xenon exposure level (10, 20, 40, 80, and 160 AFU´s) as shown in Table 9. All of the independent variables had a significant influence on the extent of fading or percentage change in whiteness; however, the influence was confounded by interactions between them. Significant interactions included FWA x concentration, FWA x exposure, and concentration x exposure. The third order interaction FWA x concentration x exposure was not significant. Because the second order interactions between the independent variables were significant, generalizations about the effects of FWA

Table 9. Analysis of Variance for Mean Percentage Change in Whiteness of the FWA Treatments

Source of Variation	Degrees of Freedom	Sum of Squares	F-Value	PR>F
FWA	8	14934.66	39.23	0.0001*
Concentration	2	6063.82	63.72	0.0001*
Exposure	4	156885.47	824.30	0.0001*
FWA x Conc.	16	18037.11	23.69	0.0001*
FWA x Expos.	32	3944.44	2.59	0.0001*
Conc. x Expos.	8	3857.58	10.13	0.0001*
FWA x Conc. x Expos.	64	1498.30	0.49	0.9990

* Significant at the 0.01 level.

FWA: 1-9
Concentration: 0.05, 0.50, 1.0% owf
Exposure: 10, 20, 40, 80, 160 AFU´s

Table 10. Analysis of Variance for Mean Percentage Change in Whiteness of the FWA Treatments at the 0.05% owf Concentration

Source of Variation	Degrees of Freedom	Sum of Squares	F-Value	PR>F
FWA	8	5064.46	59.66	0.0001*
Exposure	4	34130.03	804.13	0.0001*
FWA x Exposure	32	324.30	0.96	0.5483

* Significant at the 0.01 level.

FWA: 1-9
Exposure: 10, 20, 40, 80, 160 AFU´s

type, concentration, and xenon exposure on changes in whiteness or fading must be made judiciously.

An additional ANOVA was carried out to determine if percentage change in whiteness was influenced by FWA type or exposure at the 0.05% concentration only (see Table 10). Both FWA type and exposure were significant, whereas the interaction between the two (FWA x exposure) was not.

The results of the Duncan's Multiple Range Test for FWA type showed that overall, FWA's 8, 4, 5, and 9 had significantly higher percentage changes in whiteness (computed over all FWA concentrations and xenon exposure levels) or the greatest amount of fading after exposure (see Table 11 and Figure 4). The grand means for these FWA's were -88.4%, -87.6%, -85.2%, and -83.9%, respectively. Conversely, FWA's 1, 2, and 6 experienced the least amount of change in whiteness overall, although the loss was still substantial. The grand means associated with these FWA's (i.e., -68.6%, -70.2%, and -71.9%) were appreciably lower than those associated with the other FWA types.

This analysis of the grand means for FWA type only applies to selected concentrations and exposure levels because of the significance of the interactions between the variables. The rank order and significant differences among the FWA's varied, depending on concentration and xenon exposure level. These specific interactions will be discussed following the main effects.

Based on the Duncan's Multiple Range Test on the means for percentage change in whiteness for FWA type at the 0.05% owf concentration level (see Table 12 and Figure 4), FWA's 9 and 7

Table 11. Duncan´s Multiple Range Test on Mean Percentage Change in Whiteness for FWA Types

FWA	Mean Change in Whiteness, %	Grouping*
8	-88.4	A
4	-87.6	A B
5	-85.2	A B
9	-83.9	B
7	-76.2	C
3	-73.2	C D
6	-71.9	D E
2	-70.2	D E
1	-68.6	E

* Means with the same letter are not significantly different at the 0.05 level.

Table 12. Duncan´s Multiple Range Test on Mean Percentage Change in Whiteness for FWA Types at 0.05% owf Concentration

FWA	Mean Change in Whiteness, %	Grouping*
9	-88.2	A
7	-80.5	B
2	-72.5	C
6	-71.7	C
1	-69.9	C D
5	-68.0	D E
8	-65.6	E F
3	-65.3	E F
4	-64.0	F

* Means with the same letter are not significantly different at the 0.05 level.

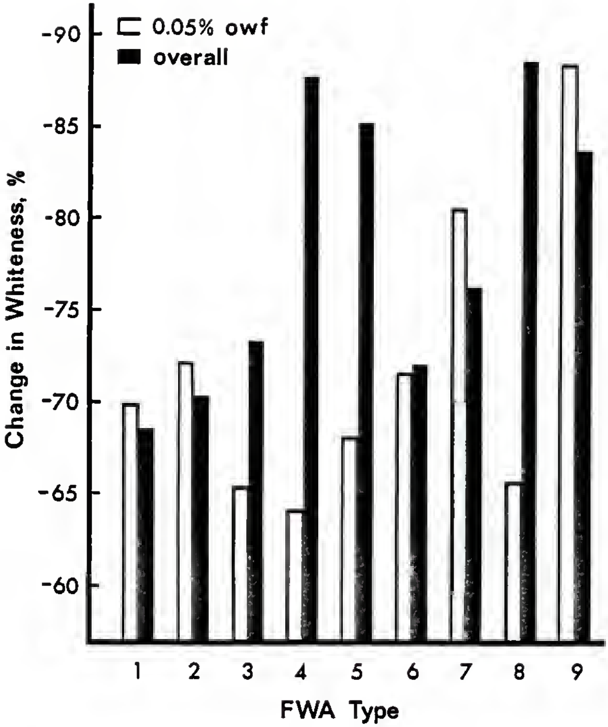


Figure 4. Mean Percentage Change in Whiteness for FWA Types Overall and at the 0.05% owf Concentration.

exhibited the greatest amount of fading overall with means for change in whiteness of -88.2% and -80.5%, respectively. The least amount of change in whiteness was associated with FWA's 4, 3, and 8 with values of -64.0%, -65.4%, and -65.6%.

Based on the Duncan's Multiple Range Test for concentration, the grand mean percentage change in whiteness for the 0.05% owf treatments (-71.8%) was significantly lower than the means for 0.50 and 1.0% owf, thus indicating that, overall, changes in whiteness or fading were often less at the lowest concentration (see Table 13). However, there was no significant difference between the grand means for the 0.50 and 1.0% owf concentrations with decreases in whiteness of -80.8% and -82.6%, respectively.

Table 13. Duncan's Multiple Range Test on Mean Percentage Change in Whiteness for FWA Concentrations

Concentration (% owf)	Mean Change in Whiteness, %	Grouping*
1.0	-82.6	A
0.50	-80.8	A
0.05	-71.8	B

* Means with the same letter are not significantly different at the 0.05 level.

As mentioned previously, the effects of concentration were confounded by second order interactions with FWA type and xenon exposure. Hence, any generalizations concerning the influence of concentration on fading or percentage change in whiteness are restricted to specific treatment combinations, and must be viewed in relation to the differences in the theoretical versus actual concentrations of the FWA's.

Duncan's Multiple Range Test on xenon exposure levels for the overall means are shown in Table 14. There was a significant difference between the means for percentage change in whiteness at the five xenon exposure levels. The loss in whiteness increased progressively up to 80 AFU's and then began to level off. An appreciable amount of fading occurred in the FWA's after only 10 and 20 AFU's of xenon exposure with overall grand means for percentage change in whiteness of -43.1% and -61.0%, respectively. At 80 and 160 AFU's of xenon exposure, the loss exceeded 100% with corresponding means of -100.2% and -108.1%. This dose signify that something other than just loss of fluorescence was occurring.

The results of the Duncan's Multiple Range Test on exposure level for the 0.05% owf concentration only are shown in Table 15. The loss in whiteness increased progressively between 10, 20, 40, and 80 AFU's but began to level off between 80 and 160 AFU's. The means ranged from -42.7 to -96.6% with no exposure exceeding 100%.

Table 14. Duncan´s Multiple Range Test on Mean Percentage Change in Whiteness for Xenon Exposure Levels

Exposure (AFU´s)	Mean Change in Whiteness, %	Grouping*
160	-108.1	A
80	-100.2	B
40	-79.4	C
20	-61.0	D
10	-43.1	E

* Means with the same letter are not significantly different at the 0.05 level.

Table 15. Duncan´s Multiple Range Test on Mean Percentage Change in Whiteness for Xenon Exposure Levels at 0.05% owf Concentration

Exposure (AFU´s)	Mean Change in Whiteness, %	Grouping*
160	-96.6	A
80	-87.4	B
40	-73.8	C
20	-58.2	D
10	-42.7	E

* Means with the same letter are not significantly different at the 0.05 level.

The FWA x concentration interaction was significant with means given in Table 16 and results of the Duncan's Multiple Range Test shown in Table 17. The rank order of the FWA means for percentage change in whiteness overall and at the 1.0% owf concentration were almost identical and were similar to those for the 0.50% owf concentration. However, the overall means varied considerably from the rank order of the FWA means at the 0.05% owf concentration, especially for FWA 4.

Table 16. Mean Percentage Change in Whiteness for FWA Types at Each Concentration

	Change in Whiteness, %		
	Concentration (% owf)		
FWA	0.05	0.50	1.0
1	-69.9	-69.4	-66.5
2	-72.5	-70.2	-67.8
3	-65.3	-76.3	-78.2
4	-64.0	-96.6	-102.2
5	-68.0	-90.0	-97.6
6	-71.7	-73.4	-70.6
7	-80.5	-75.8	-72.4
8	-65.6	-92.2	-107.5
9	-88.2	-83.0	-80.4

As mentioned previously, because of the self-extinguishing effect that occurred with excessive concentrations of selected FWA's, it was difficult to compare the fading characteristics of the FWA's at the higher concentrations. Hence, the rank order of the grand means for

Table 17. Duncan's Multiple Range Test on Mean Percentage Change in Whiteness for FWA Types at Each Concentration

FWA	Concentration (% owf)	Mean Change in Whiteness, %	Grouping*
8	1.0	-107.5	A
4	1.0	-102.2	A B
5	1.0	-97.6	B C
4	0.50	-96.6	B C
8	0.50	-92.2	C D
5	0.50	-90.0	D
9	0.05	-88.2	D E
9	0.50	-83.0	E F
7	0.05	-80.5	F G
9	1.0	-80.4	F G
3	1.0	-78.2	F G H
3	0.50	-76.3	F G H I
7	0.50	-75.8	G H I
6	0.50	-73.4	H I J
2	0.05	-72.6	H I J K
7	1.0	-72.5	H I J K
6	0.05	-71.8	H I J K
6	1.0	-70.6	I J K L
2	0.50	-70.2	I J K L
1	0.05	-69.9	I J K L
1	0.50	-69.4	I J K L
5	0.05	-68.0	J K L
2	1.0	-67.8	J K L
1	1.0	-66.5	J K L
8	0.05	-65.6	K L
3	0.05	-65.3	K L
4	0.05	-64.0	L

* Means with the same letter are not significantly different at the 0.05 level.

FWA type in Table 11 is heavily biased by the data for the 0.50 and 1.0% owf concentrations.

The FWA x exposure interaction also was significant with overall means and the Duncan's Multiple Range Test results shown in Tables 18 and 19. For the majority of the FWA treatments, loss in whiteness increased significantly with increasing xenon exposure level. An appreciable amount of fading occurred in the FWA's after only 10 and 20 AFU's of xenon exposure with overall grand means for percentage change in whiteness of -43.1% and -61.0%. At 80 and 160 AFU's, some of the FWA's exhibited losses in whiteness which exceeded 100% (FWA's 4, 5, 8, and 9 at 80 AFU's and all FWA's except 1 and 2 at 160 AFU's), indicating that both yellowing and loss of fluorescence had occurred.

Table 18. Mean Percentage Change in Whiteness for FWA Types at Each Xenon Exposure Level

	Change in Whiteness, %				
	Exposure (AFU's)				
FWA	10	20	40	80	160
1	-37.1	-52.8	-68.6	-87.3	-97.0
2	-38.2	-53.2	-71.7	-89.9	-98.1
3	-38.9	-56.6	-73.4	-95.2	-102.2
4	-43.4	-64.2	-86.8	-114.4	-129.3
5	-45.9	-66.0	-86.0	-112.0	-116.0
6	-37.7	-54.6	-72.6	-94.5	-100.2
7	-45.2	-61.6	-77.8	-95.1	-101.7
8	-47.6	-68.9	-89.8	-112.8	-122.9
9	-54.2	-71.6	-87.4	-100.8	-105.6

Table 19. Duncan's Multiple Range Test on Mean Percentage Change in Whiteness for FWA Types at Each Xenon Exposure Level

FWA	Exposure (AFU's)	Mean Change in Whiteness, %	Grouping*
4	160	-129.3	A
8	180	-122.9	A B
5	160	-118.0	B C
4	80	-114.4	C
8	80	-112.8	C D
5	80	-112.0	C D
9	160	-105.6	D E
3	180	-102.2	E F
7	160	-101.7	E F
9	80	-100.8	E F
6	180	-100.2	E F
2	160	-98.1	E F G
1	160	-97.0	E F G
3	80	-95.2	F G H
7	80	-95.1	F G H I
6	80	-94.5	F G H I
2	80	-89.9	G H I
8	40	-89.8	G H I
9	40	-87.4	H I
1	80	-87.4	H I
4	40	-86.8	H I
5	40	-86.0	I
7	40	-77.8	J
3	40	-73.4	J K
6	40	-72.6	J K
2	40	-71.7	J K
9	20	-71.6	J K
8	20	-68.9	J K L
1	40	-68.6	K L
5	20	-68.0	K L
4	20	-64.2	K L M
7	20	-61.8	L M N
3	20	-56.6	M N O
6	20	-54.6	N O P
9	10	-54.2	N O P
2	20	-53.2	N O P Q
1	20	-52.8	N O P Q
8	10	-47.6	O P Q R
5	10	-45.9	P Q R S
7	10	-45.2	Q R S
4	10	-43.4	R S
3	10	-38.9	R S
2	10	-38.2	S
8	10	-37.7	S
1	10	-37.2	S

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* Means with the same letter are not significantly different at the 0.05 level.

Many of the FWA's had fading rate curves similar to dyes in that greater color change occurred initially and then the rate of fade leveled off as xenon exposure continued. This effect is illustrated by the rate-of-fade curves in Figure 5, constructed from the exposure level grand means for percentage change in whiteness, overall and at the 0.05% owf concentration.

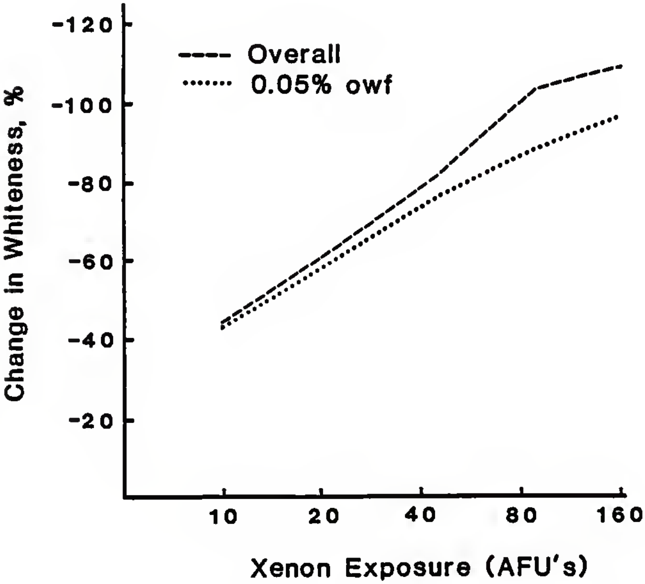


Figure 5. Rate of Fade Curves for FWA's Based on the Exposure Level Grand Means for Percentage Change in Whiteness Overall and at the 0.05% owf Concentration.

At the 0.05% owf concentration, the means for percentage change in whiteness for the five exposure levels ranged from -33.2% to -63.2% at 10 AFU´s, -49.4% to -79.6% at 20 AFU´s, -64.8% to -92.0% at 40 AFU´s, -80.4% to -100.2% at 80 AFU´s, and -90.6% to -106.1% at 160 AFU´S (see Table 20). All of the FWA´s, except FWA 4 (-49.4%) lost more than 50% of their initial increase in whiteness after 20 AFU´s. After 160 AFU´s, most of the FWA´s had faded completely and retained less than 10% of their original increase in whiteness. The appreciable changes in whiteness after 10 AFU´s reflected that, in general, FWA´s have poor lightfastness. Furthermore, based on the ranges for the five exposure levels as given above, low levels of xenon exposure are more suitable for evaluating differences among the lightfastness properties of FWA´s which has implications for future lightfastness studies.

Table 20. Mean Percentage Change in Whiteness for FWA Type and Xenon Exposure Level at 0.05% owf Concentration

	Change in Whiteness, %				
	Exposure (AFU´s)				
FWA	10	20	40	80	160
1	-39.2	-55.0	-72.9	-85.8	-96.7
2	-43.0	-58.2	-75.0	-88.3	-98.0
3	-36.7	-52.0	-66.4	-80.9	-90.6
4	-33.2	-49.4	-64.8	-81.0	-91.4
5	-39.4	-53.2	-68.8	-85.2	-93.3
6	-41.2	-56.9	-73.2	-89.2	-98.1
7	-52.0	-68.2	-83.6	-95.6	-103.0
8	-36.4	-51.6	-67.0	-80.4	-92.4
9	-63.2	-79.6	-92.0	-100.2	-106.1

The concentration x exposure interaction was significant, and the overall grand means and Duncan's Multiple Range Test results are given in Tables 21 and 22. There was no significant difference among the percentage change in whiteness means for the three concentration levels at 10 AFU's. At 10, 20, and 40 AFU's of exposure, the concentration means were in order of increasing exposure. However, the rank order of the concentration means varied at 80 and 160 AFU's of xenon exposure.

Table 21. Mean Percentage Change in Whiteness for Xenon Exposure Levels at Each Concentration

Exposure (AFU's)	Change in Whiteness, %		
	Concentration (% owf)		
	0.05	0.50	1.0
10	-42.7	-41.8	-44.9
20	-58.2	-60.6	-64.4
40	-73.8	-79.9	-84.4
80	-87.4	-109.8	-103.5
160	-96.6	-112.0	-115.8

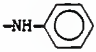
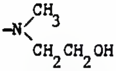
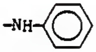
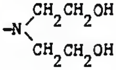
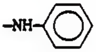
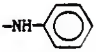
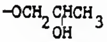
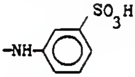
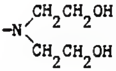
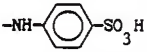
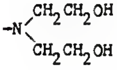
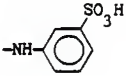
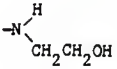
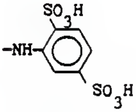
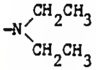
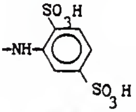
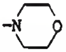
Table 22. Duncan's Multiple Range Test on Mean Percentage Change in Whiteness for FWA Concentrations at Each Xenon Exposure Level

Exposure (AFU's)	Concentration (% owf)	Mean Change in Whiteness, %	Grouping*
160	1.0	-115.8	A
160	0.50	-112.0	A B
80	0.50	-109.8	B
80	1.0	-103.5	C
160	0.05	-96.6	D
80	0.05	-87.4	E
40	1.0	-84.4	E F
40	0.50	-79.9	F
40	0.05	-73.8	G
20	1.0	-64.4	H
20	0.50	-60.6	H I
20	0.05	-58.2	I
10	1.0	-44.9	J
10	0.05	-42.7	J
10	0.50	-41.8	J

* Means with the same letter are not significantly different at the 0.05 level.

The percentage change in whiteness of the FWA-treated cotton was influenced by many factors, including actual versus theoretical concentration, initial whiteness value due to application of the FWA (ΔWI´), xenon exposure level, and chemical structure. The relationship between the actual concentration of the FWA's at the 0.05% owf level, the initial whiteness values of the FWA's, and chemical structures of the X and Y functional groups on the parent triazinylamino stilbene structure are illustrated in Table 23.

Table 23. Comparison of Actual Concentration, FWA Type, Whiteness Index, Change in Whiteness (ΔWI′, ΔWI, and Percent), and Functional Groups at the 0.05% owf Theoretical Concentration

Actual Conc. (% owf)	FWA	Means*			Change in WI (%)	Functional Groups	
		WI	ΔWI′	ΔWI		X	Y
0.05	5	114.2	33.0	-22.4	-68.0		 $-N\begin{matrix}CH_3\\CH_2CH_2OH\end{matrix}$
	8	117.2	35.8	-23.5	-65.6		 $-N\begin{matrix}CH_2CH_2OH\\CH_2CH_2OH\end{matrix}$
0.04	4	124.1	42.8	-27.4	-64.0		$-OCH_3$
	3	112.8	31.4	-20.5	-65.3		 $-OCH_2\underset{OH}{CH}CH_3$
	1	109.1	27.8	-19.4	-69.9		 $-N\begin{matrix}CH_2CH_2OH\\CH_2CH_2OH\end{matrix}$
	2	106.4	25.0	-18.2	-72.5		 $-N\begin{matrix}CH_2CH_2OH\\CH_2CH_2OH\end{matrix}$
0.03	8	113.6	32.2	-23.1	-71.7		 $-N\begin{matrix}H\\CH_2CH_2OH\end{matrix}$
0.02	9	100.8	19.4	-17.2	-88.2		 $-N\begin{matrix}CH_2CH_3\\CH_2CH_3\end{matrix}$
	7	108.4	26.2	-21.9	-80.5		

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* Grand means for xenon exposure based on cell means for 10, 20, 40, 80, and 160 AFU′s.

As previously mentioned, the actual concentration of the FWA´s at the 0.05% theoretical level were 0.02 (FWA´s 7 and 9), 0.03 (FWA 6), 0.04 (FWA´s 1-4), and 0.05% (FWA´s 5 and 8) owf. FWA´s 7 and 9 had the highest mean percentage change in whiteness (based on the cell means for the five exposure levels) at the 0.05% owf application level, compared to the other FWA types; but they also had the lowest actual concentration (0.02% owf). They also exhibited the greatest percentage reduction in whiteness (or the greatest fading) at each xenon exposure level (see Table 20). FWA 9 was the least effective fluorescent compound (i.e., had the lowest WI value after application) and had the highest mean loss in whiteness (-88.2%), compared to all of the FWA´s evaluated, including FWA 7 which also had a 0.02% owf actual concentration. In addition, FWA 9 also had the greatest percentage loss in whiteness at each exposure level. Similarly, FWA 7 had the second greatest loss in whiteness at all xenon exposure levels. Based on the chemical structure of the functional groups, FWA´s 7 and 9 both had disulfonated anilino groups in the X position which may account for the lower actual concentrations (0.02% owf), but differed in the Y group. Perhaps the diethyl amino group in the Y position restricted both exhaustion and fluorescence because it lacked polar -OH groups which could hydrogen bond with the hydroxyl groups on cellulose or which contain the more easily excited free electron pairs which often facilitate absorption of UV and visible electromagnetic radiation.

The initial whiteness index of the samples treated with FWA 7 (WI = 108.4) at an actual concentration of 0.02% owf was comparable to that obtained for FWA's 1 and 2 (109.1 and 106.4) even though twice the amount was present (0.04% owf). However, the grand means for percentage change in whiteness for these FWA's was appreciably less (-69.9% and -72.5%) than FWA 7, but greater than that observed for the FWA's with actual concentrations of 0.04% and 0.05% owf. The functional groups on FWA's 1 and 2 differed from FWA 7 in that they contained dihydroxyethyl amino groups in the Y position and only one sulfonic acid group on the anilino nucleus in the meta (FWA 1) and para (FWA 2) positions, which probably were responsible for the higher concentration compared to FWA 7.

At all xenon exposure levels (except 80 and 160 AFU's), FWA 2 ranks third in terms of percentage loss in whiteness and was preceded only by FWA's 9 and 7 which had the greatest change in whiteness. As mentioned above, the only difference between the X and Y functional groups for FWA's 1 and 2 was in the position of the sulfonic acid group on the anilino or X functional group. Thus, the location of the sulfonic acid group in the para position (FWA 2) may slightly hinder fluorescence and increase fading in FWA's. Previous research has shown that electron donating (-NHR) and electron withdrawing $(-SO_3H)$ groups in the para positions on a benzene ring decreases fluorescence (91).

At all xenon exposure levels, the percentages for change in whiteness and grand means associated with FWA 6 were comparable to those obtained for FWA 2; however, FWA 6 had a slightly lower actual concentration (0.03% owf) and its initial WI value was greater (WI = 113.6), indicating that it imparted appreciably more whiteness, compared to FWA's 9 (lowest WI), 2, 7, and 1. The sulfonic acid groups on the anilino structure in FWA 6 also was in the more favorable meta position, which may further support the above theory; however it differed from FWA 1 in that it contained a monohydroxyethyl amino group in the Y position on the triazinylamino stilbene parent structure.

Overall, FWA's 4, 3, 8, and 5 exhibited the least amount of fading during xenon exposure with means for percentage change in whiteness of -64.0%, -65.3%, -65.6%, and -68.0%, respectively. Except for FWA 6, these FWA's also had the highest WI values before exposure (i.e., 124.1, 112.8, 117.2, and 114.2, respectively). Both the chemical structure of the FWA's and actual amount applied (0.05% owf for FWA's 5 and 8, and 0.04% for FWA's 4 and 3) influenced the loss in whiteness. Unlike all of the other FWA's evaluated, FWA's 3, 4, 5, and 8 did not have water solubilizing sulfonic acid groups on the anilino functional group in the X position which probably was responsible for the higher exhaustion rates. FWA 4 exhibited the greatest increase in whiteness (WI = 124.1), compared to all other FWA's, the lowest change in whiteness overall (-64.0%), and was among those FWA's that exhibited the least amount of fading within each of the five xenon exposure levels. FWA's 4 and 3 both had oxygen containing Y groups, rather than mono- or dihydroxyethyl amino groups in the Y position. Hence, the methoxy group may be responsible for the greater whiteness (WI = 124.1) and resistance to fading of FWA 4, compared to the other FWA's evaluated. Previous research has shown that alkoxy groups, especially methoxy groups, increase both fluorescence intensity and the lightfastness of FWA's (22,35,42,91).

In summary, the whiteness of the FWA-treated cotton progressively decreased with increasing xenon exposure. The percentage change in whiteness ranged from -33.2% to -155.8%. Values above 100% were observed suggesting that things, other than just fading of the whitening effect, were occurring. Overall, FWA's 8, 4, 5, and 9 had significantly higher percentage changes in whiteness (with values ranging from -88.4% to -83.9%), while FWA's 1, 2, and 6 had the least amount of change in whiteness (values ranged from -68.6% to -71.9%). At the 0.05% owf concentration only, FWA's 9 and 7 exhibited the greatest fading (-88.2% and -80.5%, respectively), while FWA's 4, 3, and 8 had the least amount of change in whiteness (-64.0%, -65.4%, and -65.6%, respectively). The 0.05% owf concentration had the lowest percentage change in whiteness (-71.8%), compared to the other theoretical concentrations. The 1.0% owf concentration had the greatest amount of change in whiteness (-82.6%), although not significantly different from the 0.50% owf concentration. As expected the percentage change in whiteness of the FWA-treated cotton increased (overall and at the 0.05% owf concentration only) progressively up to 80 AFU's and then leveled off. As the magnitude of the difference between exposure levels increased, so did the difference in change in whiteness, up to 80 AFU's.

The percentage change in whiteness of the FWA-treated cotton was influenced by many factors including the actual concentration present, initial whiteness imparted, xenon exposure level, and chemical structure. Generally, at the 0.05% owf theoretical concentration, as the actual concentration of FWA on the fabric increased, the percentage change in whitenses decreased. Increases in actual concentration did not always correspond to increases in initial whiteness imparted, due to the influence of FWA chemical structure. Sulfonic acid groups (which are electron withdrawing) tended to decrease fluorescence intensity and influenced the initial whitenses imparted. As the number of sulfonic acid groups on the anilino structure in the X position increased, the initial whiteness and exhaustion decreased, while percentage change in whiteness or fading increased. Although this could be due to either the lower initial whitenses or less FWA on the fabric, it is most likely a combination of the two. Within the FWA's having the same actual concentration, those which had an oxygen linkage between the parent molecule and the Y functional group had increased initial whiteness imparted by the FWA and the least amount of fading or percentage change in whiteness overall.

Changes in Relative Fluorescence Intensity

The relative fluorescence intensity values (F) for each replica of the experiment, based on 3 readings per specimen, are presented in Table A3, Appendix A. Changes in relative fluorescence intensity (ΔF) were computed based on the difference between the fluorescence intensity values of the FWA-treated samples before and after xenon exposure ($\Delta F = F_{exposed} - F_{unexposed}$). The mean change in relative fluorescence intensity (ΔF) for each replica of the experiment at the five xenon exposure levels are presented in Table A7, Appendix A. The grand means for change in fluorescence intensity, which were computed on the replica means, are presented in Table 24.

The means for change in relative fluorescence intensity (ΔF) associated with the FWA treatments and untreated controls ranged from 0.00 (untreated controls) to -0.83 (FWA 9, 0.50% owf at 160 AFU's) with a negative value denoting a loss in fluorescence. The untreated control samples exhibited minimal fluorescence both initially and after xenon exposure with no changes in fluorescence intensity after exposure being reported. All of the FWA's, except FWA 6 at the 0.50% owf concentration level between 80 and 160 AFU's, showed a progressively greater loss in fluorescence with exposure.

As in the change in whiteness index (ΔWI) data, incorrect conclusions can be drawn from only the differences in relative fluorescence intensity (ΔF) before and after xenon exposure because the amount of change possible was primarily determined by the initial fluorescence intensity value ($\Delta F'$) after the FWA's were applied to the cotton fabric. These values are shown in Table 5, and ranged from

Table 24. Mean Change in Relative Fluorescence Intensity (ΔF) at Each Xenon Exposure Level

FWA	Concentration (% owf)	Change in Relative Fluorescence Intensity, ΔF				
		Exposure (AFU's)				
		10	20	40	80	160
Control	0.0	0.00	0.00	0.00	0.00	0.00
1	0.05	−0.18	−0.23	−0.34	−0.45	−0.55
	0.50	−0.26	−0.36	−0.46	−0.60	−0.68
	1.0	−0.26	−0.34	−0.44	−0.53	−0.62
2	0.05	−0.21	−0.28	−0.38	−0.48	−0.58
	0.50	−0.20	−0.34	−0.46	−0.58	−0.68
	1.0	−0.26	−0.34	−0.44	−0.52	−0.61
3	0.05	−0.16	−0.26	−0.36	−0.45	−0.53
	0.50	−0.25	−0.36	−0.44	−0.60	−0.60
	1.0	−0.25	−0.34	−0.41	−0.49	−0.55
4	0.05	−0.22	−0.36	−0.42	−0.52	−0.60
	0.50	−0.22	−0.34	−0.41	−0.53	−0.57
	1.0	−0.20	−0.28	−0.38	−0.42	−0.47
5	0.05	−0.22	−0.30	−0.40	−0.52	−0.58
	0.50	−0.32	−0.44	−0.50	−0.67	−0.67
	1.0	−0.32	−0.42	−0.50	−0.59	−0.62
6	0.05	−0.24	−0.32	−0.42	−0.53	−0.63
	0.50	−0.25	−0.41	−0.50	−0.72	−0.70
	1.0	−0.26	−0.37	−0.46	−0.56	−0.64
7	0.05	−0.27	−0.34	−0.47	−0.58	−0.68
	0.50	−0.36	−0.46	−0.54	−0.74	−0.80
	1.0	−0.36	−0.46	−0.56	−0.66	−0.77
8	0.05	−0.26	−0.35	−0.43	−0.53	−0.63
	0.50	−0.28	−0.42	−0.48	−0.62	−0.67
	1.0	−0.23	−0.36	−0.43	−0.51	−0.54
9	0.05	−0.28	−0.37	−0.48	−0.58	−0.64
	0.50	−0.32	−0.44	−0.56	−0.76	−0.83
	1.0	−0.34	−0.46	−0.58	−0.68	−0.79

0.69 to 1.08. In order to compare the difference in relative fluorescence intensity of the FWA-treated samples due to the effects of xenon exposure, it was necessary to compute percentage change in the initial relative fluorescence intensity as shown:

$$\begin{array}{l}\text{\% Change in Relative}\\ \text{Fluorescence Intensity}\end{array} = \frac{\Delta F}{\Delta F'} \times 100$$

where:

$$\Delta F = F_{\substack{\text{exposed}\\ \text{FWA-treated}}} - F_{\substack{\text{unexposed}\\ \text{FWA-treated}}}$$

$$\Delta F' = F_{\substack{\text{unexposed}\\ \text{FWA-treated}}} - F_{\substack{\text{unexposed}\\ \text{untreated control}}}$$

Because some of the FWA treatments at the higher concentrations (0.50% and 1.0% owf) exceeded the optimum amount for maximum fluorescence and exhibited yellowing/self-extinguishment, these data are not suitable for studying precise relationships between concentration, fluorescence effectiveness, lightfastness, etc., as previously reported. Hence, the discussion will focus on data for the FWA-treatments at the 0.05% owf theoretical concentrations.

The data for percentage change in relative fluorescence intensity for the 27 FWA treatments (9 FWA's and 3 concentrations) at five xenon exposure levels are given in Table 25. The corresponding changes for each replication of the study are shown in Table A8, Appendix A.

Analysis of variance (ANOVA) procedures were used to evaluate the effect of FWA, concentration, and xenon exposure on percentage change in relative fluorescence intensity based on the 27 FWA treatments as

Table 25. Mean Percentage Change in Relative Fluorescence Intensity at Each Xenon Exposure Level

FWA	Concentration (% owf)	Change in Relative Fluorescence Intensity, % Exposure (AFU's) 10	20	40	80	160
1	0.05	-24.0	-29.8	-43.8	-58.4	-70.8
	0.50	-26.1	-35.4	-45.8	-58.7	-67.1
	1.0	-26.6	-34.6	-43.6	-52.9	-61.4
2	0.05	-27.7	-36.0	-49.1	-63.5	-75.2
	0.50	-20.2	-34.8	-46.8	-58.8	-69.1
	1.0	-26.6	-34.8	-44.4	-53.8	-62.3
3	0.05	-19.0	-32.5	-43.6	-53.8	-63.4
	0.50	-26.4	-37.6	-45.9	-62.6	-63.6
	1.0	-27.8	-38.0	-44.8	-53.6	-59.9
4	0.05	-22.7	-36.3	-43.6	-52.6	-61.0
	0.50	-24.8	-38.1	-45.6	-59.3	-63.4
	1.0	-24.6	-35.1	-41.2	-50.8	-57.6
5	0.05	-25.2	-34.2	-45.8	-58.8	-66.4
	0.50	-31.3	-43.0	-49.4	-65.4	-65.8
	1.0	-32.2	-41.8	-50.3	-58.9	-62.0
6	0.05	-27.6	-37.0	-48.9	-60.4	-71.6
	0.50	-24.6	-39.4	-48.3	-69.3	-67.0
	1.0	-26.4	-37.2	-46.6	-55.8	-63.8
7	0.05	-33.2	-41.2	-57.5	-71.8	-83.8
	0.50	-34.2	-43.9	-51.9	-71.2	-76.6
	1.0	-33.1	-42.6	-52.6	-61.9	-71.6
8	0.05	-27.1	-37.0	-45.4	-55.8	-66.3
	0.50	-28.0	-42.0	-47.4	-61.2	-66.2
	1.0	-25.2	-39.6	-46.6	-55.6	-58.8
9	0.05	-39.9	-53.8	-70.2	-83.4	-91.7
	0.50	-33.8	-46.8	-59.3	-80.5	-87.0
	1.0	-34.8	-47.0	-58.0	-68.8	-79.0

shown in Table 26. All of the independent variables had a significant influence on the percentage change in fluorescence intensity. The FWA x concentration, FWA x exposure, and concentration x exposure interactions were significant. The third order interaction among the variables was not significant. This same test was conducted on the 0.05% owf concentration only as shown in Table 27. FWA type and exposure were both significant, as well the interaction between the two variables at this concentration.

The results of the Duncan's Multiple Range Test for FWA type based on three concentrations are shown in Table 28, and the corresponding statistics for the 0.05% owf concentration are given in Table 29. Overall and at the 0.05% concentration, FWA's 9 and 7 had the greatest loss of fluorescence intensity after xenon exposure, while FWA's 1, 3, and 4 exhibited the least reduction. The rank order and significant differences between FWA's 5, 6, 2, and 8 differed slightly in the two statistical tests which reflected some of the confounding interactions occurring at the higher FWA concentrations. The rank order of the grand means for percentage change in fluorescence intensity differed from those observed for changes in whiteness because of confounding interactions at the higher concentrations. However, the Duncan's Multiple Range Test results for the 0.05% owf concentration were very similar. For example, in both tests FWA's 9 and 7 exhibited significantly greater change in fluorescence than did the other FWA types followed by FWA's 2 and 6, and FWA's 3 and 4 exhibited the least amount of change. The rank order for FWA's 8, 5, and 1 differed slightly, however in many

Table 26. Analysis of Variance for Mean Percentage Change in Relative Fluorescence Intensity of the FWA Treatments

Source of Variation	Degrees of Freedom	Sum of Squares	F-Value	PR>F
FWA	8	8490.85	66.04	0.0001*
Concentration	2	496.94	15.46	0.0001*
Exposure	4	58721.31	913.47	0.0001*
FWA x Conc.	16	902.36	3.51	0.0001*
FWA x Expos.	32	958.40	1.86	0.0077*
Conc. x Expos.	8	881.17	6.85	0.0001*
FWA x Conc. x Expos.	64	347.22	0.34	1.0000

* Significant at the 0.01 level.

FWA: 1-9
Concentration: 0.05, 0.50, 1.0% owf
Exposure: 10, 20, 40, 80, 160 AFU's

Table 27. Analysis of Variance for Mean Percentage Change in Relative Fluorescence Intensity of the FWA Treatments at 0.05% owf Concentration

Source of Variation	Degrees of Freedom	Sum of Squares	F-Value	PR>F
FWA	8	5279.49	74.79	0.0001*
Exposure	4	23533.37	666.77	0.0001*
FWA x Exposure	32	484.88	1.72	0.0479**

* Significant at the 0.01 level.
** Significant at the 0.05 level.

FWA: 1-9
Exposure: 10, 20, 40, 80, 160 AFU's

Table 28. Duncan's Multiple Range Test on Mean Percentage Change in Relative Fluorescence Intensity for FWA Types

FWA	Mean Change in Relative Fluorescence Intensity, %	Grouping*
9	-62.3	A
7	-55.2	B
5	-48.7	C
6	-48.2	C
2	-46.8	C D
8	-46.8	C D
1	-45.2	D E
3	-44.8	D E
4	-43.8	E

* Means with the same letter are not significantly different at the 0.05 level.

Table 29. Duncan's Multiple Range Test on Mean Percentage Change in Relative Fluorescence Intensity for FWA Types at 0.05% owf Concentration

FWA	Mean Change in Relative Fluorescence Intensity, %	Grouping*
9	-67.8	A
7	-57.5	B
2	-50.3	C
6	-49.1	C
8	-46.3	D
5	-46.0	D
1	-45.4	D E
4	-43.2	E F
3	-42.4	F

* Means with the same letter are not significantly different at the 0.05 level.

instances there were no significant differences between their means. Hence, percentage change in fluorescence intensity was well correlated with changes in whiteness.

The greatest percentage change in fluorescence intensity occurred at the 0.50% owf concentration (-50.3%), but it was not significantly different from the grand mean for the 0.05% owf concentration and was only slightly higher but significantly different from the 1.0% owf mean (-47.2%) (see Table 30). These results did not corresponded with the ranking and significant differences among the grand means for the concentration levels associated with percentage change in whiteness. This was due to the self-extinguishment of fluorescence at high concentrations and yellowing of the fiber substrate.

The loss of fluorescence increased with increasing xenon exposure level as shown in Table 31. Greater differences were observed between the grand means for 10, 20, 40, and 80 AFU´s of xenon exposure, than occurred between 80 and 160 AFU´s, indicating that loss in fluorescence tended to level off as was observed for change in whiteness. However, the means for the 0.05% owf FWA treatments showed that the difference in percentage change in fluorescence between 10 and 20 AFU´s and between 80 and 160 AFU´s were identical, but greater change was observed between 20 and 40 AFU´s and between 40 and 80 AFU´s (see Table 32).

Table 30. Duncan´s Multiple Range Test on Mean Percentage Change in Relative Fluorescence Intensity for FWA Concentrations

Concentration (% owf)	Mean Change in Relative Fluorescence Intensity, %	Grouping*
0.50	-50.3	A
0.05	-49.8	A
1.0	-47.2	B

* Means with the same letter are not significantly different at the 0.05 level.

Table 31. Duncan´s Multiple Range Test on Mean Percentage Change in Relative Fluorescence Intensity for Xenon Exposure Levels

Exposure (AFU´s)	Mean Change in Relative Fluorescence Intensity, %	Grouping*
160	-68.6	A
80	-61.4	B
40	-48.8	C
20	-38.8	D
10	-27.9	E

* Means with the same letter are not significantly different at the 0.05 level.

Table 32. Duncan´s Multiple Range Test on Mean Percentage Change in Relative Fluorescence Intensity for Xenon Exposure Levels at 0.05% owf Concentration

Exposure (AFU´s)	Mean Change in Relative Fluorescence Intensity, %	Grouping*
160	-72.2	A
80	-62.0	B
40	-49.8	C
20	-37.6	D
10	-27.4	E

* Means with the same letter are not significantly different at the 0.05 level.

The FWA x concentration interaction was significant with the corresponding mean percentage changes in relative fluorescence intensity given in Table 33. The interaction suggests that the changes in fluorescence intensity differed for the three concentrations among the nine FWA's. The Duncan's Multiple Range Test results for the means are shown in Table 34. The initial increase in whiteness imparted to the fabric by the FWA and fluorescence effectiveness also appeared to be related to the loss in whiteness and changes in fluorescence during xenon exposure.

Table 33. Mean Percentage Change in Relative Fluorescence Intensity for FWA Types at Each Concentration

	Change in Relative Fluorescence Intensity, %		
	Concentration (% owf)		
FWA	0.05	0.50	1.0
1	-45.4	-46.6	-43.8
2	-50.3	-46.0	-44.4
3	-42.4	-47.2	-44.8
4	-43.2	-46.2	-41.9
5	-46.0	-51.0	-49.0
6	-49.1	-49.7	-46.0
7	-57.5	-55.6	-52.4
8	-46.3	-49.0	-45.2
9	-67.8	-61.6	-57.5

Table 34. Duncan's Multiple Range Test on Mean Percentage Change in Relative Fluorescence Intensity for FWA Types at Each Concentration

FWA	Concentration (% owf)	Mean Change in Relative Fluorescence Intensity, %	Grouping*
9	0.05	-67.8	A
9	0.50	-61.6	B
7	0.05	-57.5	C
9	1.0	-57.5	C
7	0.50	-55.6	C D
7	1.0	-52.4	D E
5	0.50	-51.0	E F
2	0.05	-50.3	E F G
6	0.50	-49.7	E F G H
6	0.05	-49.1	E F G H I
5	1.0	-49.0	E F G H I
8	0.50	-49.0	E F G H I
3	0.50	-47.2	F G H I J
1	0.50	-46.6	G H I J K
8	0.05	-46.3	G H I J K
4	0.50	-46.2	G H I J K
5	0.05	-46.0	H I J K L
6	1.0	-46.0	H I J K L
2	0.50	-46.0	H I J K L
1	0.05	-45.4	I J K L
8	1.0	-45.2	I J K L
3	1.0	-44.8	I J K L
2	1.0	-44.4	J K L
1	1.0	-43.8	J K L
4	0.05	-43.2	J K L
3	0.05	-42.4	K L
4	1.0	-41.9	L

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* Means with the same letter are not significantly different at the 0.05 level.

The FWA x exposure interaction for the grand means was significant. Hence, the xenon exposure level influenced the differences in fading among the FWA´s (see Table 35). Results for the Duncan´s Multiple Range Test are shown in Table 36. The means for the interation at the 0.05% owf concentration and the results for the Duncan´s Multiple Range Test are given in Tables 37 and 38. The differences between the mean percentage change in fluorescence intensity for the FWA´s was greater at 20, 40, and 80 AFU´s compared to 10 and 160 AFU´s. For example, at 80 AFU´s the mean change was -62 ± 15%, where at 160 AFU´s the mean change was -72.2 ± 10% indicating that many of the FWA´s had a more similar amount of fade at these exposure levels. In addition, the xenon exposure level influenced the rank order of some of the means, except FWA´s 9 and 7.

Table 35. Mean Percentage Change in Relative Fluorescence Intensity for FWA Types at Each Xenon Exposure Level

	Change in Relative Fluorescence Intensity, %				
	Exposure (AFU´s)				
FWA	10	20	40	80	160
1	-25.6	-33.2	-44.4	-56.6	-66.4
2	-24.8	-35.2	-46.8	-58.7	-68.8
3	-24.4	-36.0	-44.8	-56.6	-62.3
4	-24.0	-36.5	-43.4	-54.2	-60.7
5	-29.6	-39.6	-48.5	-61.0	-64.8
6	-26.2	-37.8	-47.9	-61.8	-67.5
7	-33.5	-42.6	-54.0	-68.3	-77.4
8	-26.8	-39.5	-46.5	-57.6	-63.8
9	-36.2	-49.2	-62.5	-77.6	-86.0

Table 36. Duncan's Multiple Range Test on Mean Percentage Change in Relative Fluorescence Intensity for FWA Types at Each Xenon Exposure Level

FWA	Exposure (AFU's)	Mean Change in Relative Fluorescence Intensity, %	Grouping*																			
9	180	-66.0	A																			
9	80	-77.6		B																		
7	160	-77.4		B																		
2	160	-68.8			C																	
7	80	-68.3			C																	
6	160	-67.5			C	D																
1	180	-66.4			C	D	E															
5	160	-64.8			C	D	E	F														
8	160	-63.8			C	D	E	F	G													
9	40	-62.5				D	E	F	G	H												
3	180	-62.3				D	E	F	G	H												
8	80	-61.8					E	F	G	H	I											
5	80	-61.0						F	G	H	I											
4	160	-60.7						F	G	H	I											
2	80	-58.7							G	H	I	J										
8	80	-57.8								H	I	J										
3	80	-58.6									I	J										
1	80	-56.6									I	J										
4	80	-54.2										J										
7	40	-54.0										J										
9	20	-49.2											K									
5	40	-48.5											K	L								
6	40	-47.9											K	L								
2	40	-46.8											K	L	M							
8	40	-46.5											K	L	M							
3	40	-44.8											K	L	M							
1	40	-44.4											K	L	M	N						
4	40	-43.4												L	M	N						
7	20	-42.6													M	N	O					
5	20	-39.8														N	O	P				
8	20	-39.5														N	O	P				
8	20	-37.8															O	P	Q			
4	20	-36.5																P	Q			
9	10	-38.2																P	Q			
3	20	-38.0																P	Q			
2	20	-35.2																P	Q			
7	10	-33.5																	Q	R		
1	20	-33.3																	Q	R		
5	10	-29.6																		R	S	
8	10	-26.8																			S	T
6	10	-28.2																			S	T
1	10	-25.6																			S	T
2	10	-24.8																			S	T
3	10	-24.4																			S	T
4	10	-24.0																				T

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* Means with the same letter are not significantly different at the 0.05 level.

Table 37. Mean Percentage Change in Relative Fluorescence Intensity for FWA Type and Xenon Exposure Level at 0.05% owf Concentration

	Change in Relative Fluoreecence Intensity, %				
	Exposure (AFU´s)				
FWA	10	20	40	80	160
1	-24.0	-29.8	-43.8	-58.4	-70.8
2	-27.7	-36.0	-49.1	-63.5	-75.2
3	-19.0	-32.5	-43.6	-53.8	-63.4
4	-22.7	-36.3	-43.6	-52.6	-61.0
5	-25.2	-34.2	-45.8	-58.8	-66.4
6	-27.6	-37.0	-48.9	-60.4	-71.6
7	-33.2	-41.2	-57.5	-71.8	-83.8
8	-27.1	-36.9	-45.4	-55.8	-66.3
9	-39.9	-53.8	-70.2	-83.4	-91.7

Table 38. Duncan's Multiple Range Test on Mean Percentage Change in Relative Fluorescence Intensity for FWA Type and Xenon Exposure Level at 0.05% owf Concentration

FWA	Exposure (AFU's)	Mean Change in Relative Fluorescence Intensity, %	Grouping*
9	160	-91.7	A
7	160	-83.8	B
9	80	-83.4	B
2	160	-75.2	C
7	80	-71.8	C D
6	160	-71.6	C D
1	160	-70.8	C D
9	40	-70.2	C D
5	180	-66.4	D E
8	160	-68.3	D E
2	80	-63.5	E F
3	160	-63.4	E F
4	160	-61.0	E F G
6	80	-60.4	E F G H
5	80	-58.8	F G H I
1	80	-58.4	F G H I
7	40	-57.5	F G H I
8	80	-55.8	G H I
9	20	-53.8	H I J
3	80	-53.8	H I J
4	80	-52.6	I J
2	40	-49.1	J K
6	40	-48.9	J K
5	40	-45.8	K L
8	40	-45.4	K L
1	40	-43.8	K L M
3	40	-43.6	K L M
4	40	-43.6	K L M
7	20	-41.2	L M N
9	10	-39.9	L M N O
6	20	-37.0	M N O P
8	20	-37.0	M N O P
4	20	-38.3	N O P Q
2	20	-36.0	N O P Q
5	20	-34.2	O P Q R
7	10	-33.2	O P Q R S
3	20	-32.5	P Q R S
1	20	-29.8	Q R S T
2	10	-27.7	R S T U
6	10	-27.6	R S T U
8	10	-27.1	S T U
5	10	-25.2	T U V
1	10	-24.0	T U V
4	10	-22.7	U V
3	10	-19.0	V

* Means with the same letter are not significantly different at the 0.05 level.

The concentration x exposure interaction also was significant, thus the Duncan's Multiple Range test was applied to the test means (see Tables 39 and 40). The greatest overall change in fluorescence intensity occurred at 160 AFU's of xenon exposure for the 0.05% owf concentration. At the lowest exposure level the change in fluorescence increased slightly at each increasing concentration level, whereas with the other exposure levels, except 160 AFU's, the loss in fluorescence increased appreciably between 0.05 and 0.50% owf. However, at the 1.0% owf concentration, the mean change in fluorescence intensity at each exposure either decreased or did not differ appreciably from the 0.50% owf concentration. At the 0.50% and 1.0% owf concentrations, fewer differences were observed between the means for 80 and 160 AFU's due to confounding interactions previously described.

In summary, FWA type, concentration, and xenon exposure had a significant effect on the change in relative fluorescence intensity. Interactions associated with FWA x concentration, FWA x exposure, and concentration x exposure were significant. FWA's 9 and 7 experienced the greatest change in fluorescence, whereas FWA's 3 and 4 showed the least. The 0.50% owf concentration level influenced the change in fluorescence the most but was not significantly different from the 0.05% owf concentration. The 1.0% owf concentration influenced the change in fluorescence the least. Generally, as the xenon exposure level increased the loss in fluorescence also increased.

Table 39. Mean Percentage Change in Relative Fluorescence Intensity for Xenon Exposure Levels at Each Concentration

Exposure (AFU's)	Change in Relative Fluorescence Intensity, % Concentration (% owf) 0.05	 0.50	 1.0
10	-27.4	-27.7	-28.6
20	-37.6	-40.1	-39.0
40	-49.8	-49.0	-47.6
80	-62.0	-65.2	-56.9
160	-72.2	-69.6	-64.0

Table 40. Duncan's Multiple Range Test on Mean Percentage Change in Relative Fluorescence Intensity for FWA Concentrations at Each Xenon Exposure Level

Exposure (AFU's)	Concentration (% owf)	Mean Change Relative Fluorescence Intensity, %	Grouping*
160	0.05	-72.2	A
160	0.50	-69.6	B
80	0.50	-65.2	C
160	1.0	-64.0	C D
80	0.05	-62.0	D
80	1.0	-56.9	E
40	0.05	-49.8	F
40	0.50	-49.0	F
40	1.0	-47.6	F
20	0.50	-40.1	G
20	1.0	-39.0	G
20	0.05	-37.6	G
10	1.0	-28.6	H
10	0.50	-27.7	H
10	0.05	-27.4	H

* Means with the same letter are not significantly different at the 0.05 level.

Changes in Chromaticity

Color readings (L*, a*, and b*) were taken on the untreated and FWA-treated samples following 10, 20, 40, 80, and 160 AFU's of xenon exposure. Color Change (ΔL*, Δa*, and Δb*) and color difference (ΔE) were computed at each xenon exposure level and are presented, along with the mean color readings, in Tables 41–45. The initial color change and color difference of the cotton due to the FWA treatments has been previously discussed and is shown in Table 6. Because the ΔE values for the FWA treatments appreciably differed initially, and this in turn affected the amount of color change possible during xenon exposure, color change and color difference in the exposed FWA-treated samples was based on the L*, a*, and b* values for the unexposed untreated controls as shown below:

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

where:

$$\Delta L^* = L^*_{\substack{\text{exposed}\\ \text{FWA-treated}}} - L^*_{\substack{\text{unexposed}\\ \text{untreated control}}}$$

$$\Delta a^* = a^*_{\substack{\text{exposed}\\ \text{FWA-treated}}} - a^*_{\substack{\text{unexposed}\\ \text{untreated control}}}$$

$$\Delta b^* = b^*_{\substack{\text{exposed}\\ \text{FWA-treated}}} - b^*_{\substack{\text{unexposed}\\ \text{untreated control}}}$$

The total color difference units (ΔE, CIE 1976 L*a*b*) associated with the various steps on the Gray Scale were used as a reference to evaluate color change in the untreated and FWA-treated samples after

Table 41. Influence of 10 AFU´s of Xenon Exposure on the Chromaticity of the FWA Treated Fabric

FWA	Concentration (% owf)	Chromaticity						
		L*	a*	b*	ΔL*	Δa*	Δb*	ΔE
Control	0.0	94.8	-0.8	1.0	0.0	0.0	0.0	0.0
1	0.05	94.9	0.6	-1.9	0.1	1.4	-3.0	3.3
	0.50	94.9	2.0	-3.8	0.1	2.7	-5.0	5.6
	1.0	95.0	2.1	-3.9	0.1	2.8	-5.0	5.7
2	0.05	95.0	0.4	-1.4	0.1	1.1	-2.6	2.8
	0.50	94.9	1.8	-3.7	0.1	2.6	-4.8	5.4
	1.0	94.9	1.9	-3.7	0.1	2.6	-4.8	5.4
3	0.05	94.9	1.0	-2.4	0.1	1.7	-3.6	4.0
	0.50	94.8	1.9	-3.5	0.0	2.6	-4.6	5.2
	1.0	94.8	1.8	-3.0	-0.1	2.5	-4.1	4.8
4	0.05	94.9	2.0	-4.0	0.0	2.8	-5.1	5.8
	0.50	94.7	1.8	-2.6	-0.1	2.6	-3.8	4.6
	1.0	94.7	1.4	-1.8	-0.2	2.2	-3.0	3.7
5	0.05	94.8	1.2	-2.5	0.0	1.9	-3.6	4.0
	0.50	94.8	2.1	-3.2	-0.1	2.8	-4.3	5.1
	1.0	94.8	1.9	-2.5	0.0	2.6	-3.6	4.4
6	0.05	94.8	1.0	-2.3	0.0	1.8	-3.4	3.8
	0.50	94.8	2.1	-3.9	0.0	2.8	-5.0	5.7
	1.0	94.9	2.1	-3.8	0.1	2.8	-4.9	5.6
7	0.05	94.8	0.4	-1.2	0.0	1.2	-2.4	2.6
	0.50	94.9	1.6	-3.2	0.1	2.4	-4.4	5.0
	1.0	94.9	1.8	-3.4	0.0	2.6	-4.6	5.8
8	0.05	94.9	1.4	-3.2	0.0	2.1	-4.3	4.8
	0.50	94.8	2.0	-2.8	0.0	2.7	-4.0	4.8
	1.0	94.7	1.4	-1.5	-0.1	2.2	-2.6	3.4
9	0.05	94.8	0.0	-0.2	0.0	0.6	-1.3	1.4
	0.50	94.8	0.9	-2.0	0.0	1.6	-3.2	3.6
	1.0	94.9	1.2	-2.5	0.1	2.0	-3.6	4.7

Table 42. Influence of 20 AFU'e of Xenon Exposure on the Chromaticity of the FWA Treated Fabric

FWA	Concentration (% owf)	Chromaticity						
		L*	a*	b*	ΔL*	Δa*	Δb*	ΔE
Control	0.0	94.8	-0.8	0.9	0.0	-0.1	-0.2	0.2
1	0.05	94.8	0.3	-1.2	0.0	1.0	-2.3	2.5
	0.50	94.8	1.4	-2.7	-0.1	2.2	-3.8	4.4
	1.0	94.8	1.6	-2.8	-0.1	2.3	-3.9	4.5
2	0.05	94.8	0.1	-0.8	0.0	0.8	-1.9	2.0
	0.50	94.8	1.4	-2.6	-0.1	2.1	-3.8	4.3
	1.0	94.8	1.4	-2.7	0.0	2.2	-3.8	4.4
3	0.05	94.8	0.6	-1.6	-0.1	1.3	-2.8	3.0
	0.50	94.6	1.4	-2.3	-0.2	2.1	-3.4	4.0
	1.0	94.6	1.2	-1.7	-0.3	2.0	-2.8	3.4
4	0.05	94.7	1.4	-2.8	-0.1	2.2	-4.0	4.6
	0.50	94.4	1.2	-1.2	-0.4	1.9	-2.3	3.0
	1.0	94.4	0.9	-0.6	-0.4	1.6	-1.7	2.4
5	0.05	94.8	0.7	-1.7	-0.1	1.4	-2.8	3.1
	0.50	94.6	1.3	-1.5	-0.3	2.0	-2.6	3.2
	1.0	94.5	1.2	-0.8	-0.3	1.8	-2.0	2.7
6	0.05	94.8	0.4	-1.4	-0.1	1.2	-2.6	2.8
	0.50	94.7	1.4	-2.6	-0.2	2.1	-3.7	4.2
	1.0	94.8	1.4	-2.6	-0.1	2.1	-3.7	4.2
7	0.05	94.8	0.0	-0.5	-0.1	0.6	-1.6	1.7
	0.50	94.8	0.9	-2.0	-0.1	1.6	-3.2	3.6
	1.0	94.8	1.1	-2.2	-0.1	1.8	-3.4	3.8
8	0.05	94.8	0.8	-2.0	-0.1	1.6	-3.2	3.6
	0.50	94.6	1.2	-1.4	-0.3	2.0	-2.4	3.1
	1.0	94.5	0.8	0.0	-0.4	1.4	-1.1	1.8
9	0.05	94.8	-0.5	0.3	-0.1	0.2	-0.8	0.8
	0.50	94.8	0.2	-1.0	-0.1	1.0	-2.0	2.2
	1.0	94.8	0.5	-1.3	-0.1	1.2	-2.4	2.6

Table 43. Influence of 40 AFU's of Xenon Exposure on the Chromaticity of the FWA Treated Fabric

FWA	Concentration (% owf)	Chromaticity						
		L*	a*	b*	Δ L*	Δ a*	Δ b*	Δ E
Control	0.0	94.8	-0.8	1.0	0.0	-0.2	-0.1	0.2
1	0.05	94.8	0.1	-0.3	-0.1	0.6	-1.4	1.5
	0.50	94.7	0.8	-1.6	-0.1	1.6	-2.6	3.0
	1.0	94.7	1.0	-1.7	-0.1	1.8	-2.8	3.3
2	0.05	94.8	-0.3	0.0	0.0	0.4	-1.1	1.2
	0.50	94.7	0.6	-1.2	-0.2	1.3	-2.2	2.6
	1.0	94.8	0.8	-1.3	-0.1	1.5	-2.4	2.8
3	0.05	94.8	0.2	-0.8	0.0	0.9	-1.9	2.1
	0.50	94.6	0.8	-1.0	-0.3	1.5	-2.0	2.5
	1.0	95.0	0.8	-0.5	-0.2	1.4	-1.6	2.1
4	0.05	94.6	0.9	-1.7	-0.2	1.6	-2.8	3.2
	0.50	94.3	0.6	-0.4	-0.5	1.3	-1.6	2.1
	1.0	94.3	0.4	0.8	-0.5	1.2	-0.2	1.2
5	0.05	94.8	0.2	-0.8	-0.1	0.9	-1.9	2.1
	0.50	94.4	0.7	-0.1	-0.5	1.4	-1.2	1.9
	1.0	94.3	0.4	1.0	-0.5	1.2	-2.1	2.4
6	0.05	94.8	0.0	-0.5	-0.1	0.7	-1.6	1.7
	0.50	94.6	0.7	-1.2	-0.2	1.4	-2.2	2.6
	1.0	94.6	0.8	-1.2	-0.2	1.5	-2.2	2.6
7	0.05	94.8	-0.4	0.2	-0.1	0.2	-0.8	0.8
	0.50	94.6	0.3	-0.8	-0.2	1.0	-2.0	2.2
	1.0	94.7	0.4	-0.6	-0.1	1.2	-1.8	2.2
8	0.05	94.7	0.4	-1.1	-0.1	1.1	-2.2	2.4
	0.50	94.4	0.6	0.2	-0.5	1.3	-0.9	1.6
	1.0	94.3	0.2	1.6	-0.5	0.9	0.5	1.1
9	0.05	94.8	-0.7	0.8	-0.1	0.0	-0.3	0.3
	0.50	94.7	-0.2	0.1	-0.1	0.4	-1.0	1.0
	1.0	94.7	0.0	-0.1	-0.2	0.6	-1.2	1.4

Table 44. Influence of 80 AFU´s of Xenon Exposure on the Chromaticity of the FWA Treated Fabric

FWA	Concentration (% owf)	Chromaticity						
		L*	a*	b*	ΔL*	Δa*	Δb*	ΔE
Control	0.0	94.8	−0.9	1.0	−0.1	−0.2	−0.1	0.2
1	0.05	94.8	−0.4	0.4	0.0	0.2	−0.7	0.7
	0.50	94.5	0.0	0.3	−0.3	0.6	−0.8	1.0
	1.0	94.5	0.4	−0.4	−0.4	1.1	−1.4	1.8
2	0.05	94.8	−0.6	0.5	−0.1	0.0	−0.6	0.6
	0.50	94.5	−0.2	0.6	−0.4	0.4	−0.4	0.6
	1.0	94.5	0.2	−0.1	−0.3	0.9	−1.2	1.5
3	0.05	94.8	−0.2	0.0	−0.1	0.4	−1.1	1.2
	0.50	94.2	−0.2	1.4	−0.6	0.4	0.3	0.8
	1.0	94.3	0.2	0.6	−0.6	0.8	−0.4	1.0
4	0.05	94.5	0.4	−0.5	−0.3	1.1	−1.6	2.0
	0.50	93.8	−0.4	3.0	−1.0	0.4	1.8	2.0
	1.0	93.9	−0.1	2.4	−0.9	0.6	1.2	1.6
5	0.05	94.7	−0.2	0.1	−0.2	0.4	−1.0	1.0
	0.50	93.9	−0.4	2.8	−0.9	0.2	1.6	1.8
	1.0	94.0	−0.2	2.7	−0.9	0.5	1.6	1.9
6	0.05	94.6	−0.4	0.4	−0.2	0.2	−0.7	0.8
	0.50	94.4	−0.4	1.2	−0.5	0.3	0.2	0.6
	1.0	94.4	0.2	0.1	−0.4	0.8	−1.0	1.3
7	0.05	94.7	−0.8	0.8	−0.1	0.0	−0.2	0.2
	0.50	94.6	−0.6	1.0	−0.3	0.0	0.0	0.3
	1.0	94.6	0.0	0.1	−0.3	0.6	−1.0	1.2
8	0.05	94.6	0.0	−0.2	−0.2	0.6	−1.3	1.4
	0.50	94.0	−0.3	2.6	−0.8	0.4	1.4	1.6
	1.0	94.0	−0.4	3.0	−0.8	0.4	2.0	2.2
9	0.05	94.7	−0.9	1.0	−0.2	−0.2	0.0	0.2
	0.50	94.6	−0.8	1.3	−0.3	−0.2	0.2	0.4
	1.0	94.6	−0.6	0.8	−0.2	0.1	−0.3	0.4

Table 45. Influence of 160 AFU's of Xenon Exposure on the Chromaticity of the FWA Treated Fabric

FWA	Concentration (% owf)	Chromaticity						
		L*	a*	b*	ΔL*	Δa*	Δb*	ΔE
Control	0.0	94.8	-1.0	1.0	0.0	-0.2	0.0	0.2
1	0.05	94.6	-0.8	0.8	-0.2	0.0	-0.2	0.2
	0.50	94.4	-0.3	0.8	-0.4	0.4	-0.2	0.6
	1.0	94.4	0.0	0.5	-0.5	0.6	-0.6	1.0
2	0.05	94.6	-0.8	1.0	-0.2	-0.1	-0.2	0.3
	0.50	94.5	-0.4	0.9	-0.3	0.2	-0.2	0.4
	1.0	94.4	-0.2	0.6	-0.5	0.5	-0.4	0.8
3	0.05	94.6	-0.5	0.4	-0.3	0.2	-0.6	0.7
	0.50	94.3	-0.2	1.4	-0.6	0.4	0.3	0.8
	1.0	94.2	-0.2	1.5	-0.7	0.5	0.4	0.9
4	0.05	94.4	0.0	0.2	-0.4	0.7	-0.8	1.1
	0.50	94.3	-0.4	3.4	-0.6	0.2	2.4	2.4
	1.0	93.6	-0.6	3.9	-1.2	0.1	2.8	3.0
5	0.05	94.6	-0.6	0.6	-0.2	0.1	-0.4	0.4
	0.50	94.0	-0.3	2.5	-0.9	0.4	1.4	1.7
	1.0	93.8	-0.4	3.2	-1.0	0.3	2.2	2.4
6	0.05	94.6	-0.7	0.8	-0.3	0.0	-0.2	0.4
	0.50	94.4	-0.4	1.0	-0.4	0.4	0.0	0.6
	1.0	94.4	-0.2	1.0	-0.5	0.4	-0.1	0.6
7	0.05	94.6	-1.0	1.2	-0.2	-0.2	0.0	0.2
	0.50	94.7	-0.8	1.2	-0.2	0.0	0.1	0.0
	1.0	94.6	-0.5	1.0	-0.3	0.2	-0.1	0.4
8	0.05	94.6	-0.5	0.5	-0.2	0.2	-0.6	0.6
	0.50	93.9	-0.5	3.1	-0.9	0.2	2.0	2.2
	1.0	93.8	-0.6	3.6	-1.0	0.2	2.5	2.7
9	0.05	94.6	-1.0	1.2	-0.2	-0.3	0.2	0.4
	0.50	94.7	-1.0	1.4	-0.2	-0.2	0.2	0.3
	1.0	94.5	-0.9	1.4	-0.3	-0.2	0.2	0.4

xenon exposure. AATCC (9) specifies a step 5, negligible or no change, on the Gray Scale for Color Change, as 0 ± 0.2 CIE LAB units of color difference; step 4, slightly changed, as 1.7 ± 0.3 CIELAB units; step 3, noticeably changed, as 3.4 ± 0.4 CIELAB units; step 2, considerably changed, as 6.8 ± 0.6 CIELAB units; and step 1, much changed as 13.6 ± 1.0 CIELAB units.

All of the FWA treatments initially caused an appreciable color change in the cotton fabric with the mean ΔE values ranging from 8.8 (FWA 1, 1.0% owf and FWA 5, 0.50% owf) to 3.8 (FWA 9, 0.05% owf). The color change was attributed primarily to a slight hue shift from yellow (+b) to blue (-b) which was expected. There also was a slight increase in redness, but the Δa^* values were only half as large as the Δb^* values. The ΔL^* values, on the other hand, exhibited little change as a result of the FWA treatments with all values 0.4 or less.

The untreated control samples exposed to light up to 160 AFU´s showed no noticeable color change (i.e, mean $\Delta E \leq 0.2$). In most cases, the total color difference (ΔE) for the FWA-treated samples became less as exposure increased, except FWA 4, 0.50 and 1.0% owf at 160 AFU´s, FWA 5, 1.0% owf at 160 AFU´s, FWA 8, 1.0% owf at 80 and 160 AFU´s, and FWA 9, 0.05% owf at 160 AFU´s. This decrease in color difference values indicates that the whitening effect due to the application of the FWA was reduced or fading increased as xenon exposure increased. In other words, the appearance of the FWA treated samples was reverting back to that of the unexposed untreated cotton.

As previously mentioned, FWA´s 4, 5, 8, and 9 exhibited an appreciable increase in color difference at higher xenon exposures, as a result of both fabric yellowing and fading simultaneously occurring in the samples. Hence, precise interpretation of colorimetric changes during light exposure is considerably more complex with FWA´s compared to dyes. Because ΔE values only reflect the total color difference and not the hue shift or color changes which have occurred, changes in the individual L^*, a^*, and b^* values were assessed to elucidate changes occurring in the FWA-treated samples during xenon exposure.

The greatest decreases in color difference values or fading occurred after just 10 AFU´s of xenon exposure with the values decreasing progressively following 20, 40, 80, and 160 AFU´s of exposure. The ranges in the ΔE values for the five xenon exposures were: 1.4 to 5.8 (10 AFU´s), 0.8 to 4.6 (20 AFU´s), 0.3 to 3.3 (40 AFU´s), 0.4 to 2.2 (80 AFU´s, which was an increase in the ΔE value for the same FWA at 40 AFU´s), and 0 to 3.0 (160 AFU´s, which also was an increase in the ΔE value for the same FWA at 80 AFU´s). Once again, the decrease in the total color difference values indicates that the FWA´s were fading, and the appearance of the samples was progressively approaching that of the untreated controls, except at higher exposure levels (80 and 160 AFU´s) at which point both fading and yellowing were occurring.

However, the extent and type of color change that occurred on the FWA-treated samples during xenon exposure was influenced by the actual and theoretical concentrations. At the 0.05% owf concentration level only, the ΔE values decreased as xenon exposure level increased. After 160 AFU´s the ΔE values ranged from 0.2 to 1.1 which reflects very little color difference between the untreated and FWA-treated cotton. Most of the whiteness which had initially been imparted by the FWA had faded. The initial ΔE values due to the treatment at this concentration ranged from 3.8 to 8.4. However, one must keep in mind that color difference values only reflect the total amount of color change which had occurred and give no indication of the actual change in color or hue shifts which have taken place. The actual color changes are reflected in the ΔL^*, Δa^*, and Δb^* values.

The change in the L^* value or lightness/brightness was very minimal as exposure level increased with ΔL^* values ranging from 0.1 to -1.2 with a positive value designating greater lightness/brightness and a negative value less lightness/brightness, compared to the unexposed untreated cotton. This was expected since initially the L^* value increased just slightly due to the application of the FWA with ΔL^* values ranging from 0.1 to 0.4. It appears that this very slight initial increase was lost after exposure, with the result of a very slight decrease in lightness/brightness. Hence, the majority of the color difference (ΔE) was attributed to changes in the a^* and b^* components.

The a^* and Δa^* values became smaller as xenon exposure level increased, reflecting a decrease in redness and an increase in greenness. As previously mentioned the application of the FWA to the cotton caused a shift from green to red ($-a^*$ to $+a^*$) on the cotton fabric with Δa^* values of the FWA-treated samples ranging from 1.6 to 4.3. After xenon exposure the Δa^* values ranged from 2.8 to 0.6 at 10 AFU´s, 1.3 to 0.2 at 10 AFU´s, 1.8 to 0 at 40 AFU´s, 1.1 to -0.2 at

80 AFU´s, and 0.7 to −0.3 at 160 AFU´s.

An a* value can be positive, reflecting redness or negative (−), denoting greenness. Likewise, a positive Δ a* value greater than 0.7 would reflect redness in the FWA-treated sample. Values of Δ a* between 0.7 and 0 reflected a loss of redness and an increasing amount of greenness in the FWA-treated sample. A negative (−) Δ a* value would reflect more greenness in the FWA-treated sample than the untreated cotton.

Among the 27 treatments (9 FWA´s at 3 concentrations) at 10 AFU´s, only one treatment showed an increasing amount of greenness (and thus no redness) in its color, and at 20 AFU´s only two treatments showed an increase in greenness. After 40 AFU´s of xenon exposure, seven treatments began to increase in greenness. However, after 80 AFU´s, 22 of the treatments showed increasing greenness with two of those being greener than the untreated cotton, and at 160 AFU´s all treatments showed an increasing amount of greenness in their color with five of those being greener than the untreated cotton.

The seven treatments (FWA 2, 0.05% owf at 160 AFU´s, FWA 7, 0.05% owf at 160 AFU´s, FWA 9, 0.05, and 0.50% owf at 80 and 160 AFU´s and 1.0% at 160 AFU´s) that showed greater amounts of greenness than the unexposed untreated cotton ranged in Δ a* values from −0.1 to −0.3. These values are quite small and in comparison to the initial increases in the a* value due to the application of the FWA and seem rather unimportant. Because the instrument has variations of ±0.4 units, these differences may be due to instrumental and operator error, rather than actual color change in the samples (i.e., greater greenness than the untreated cotton). However, FWA's 9, 7, and 2 did show significantly greater losses in fluorescence and whiteness at these levels, thus the color change may be significant.

The greatest change in the Δa^* values due to xenon exposure occurred after 10 AFU's, with fading taking place at a more or less constant or decreasing rate between 20, 40, and 80 AFU's. The least amount of fading was observed between 80 and 160 AFU's, which agrees with the previous discussions that the fading of the FWA's occurred more rapidly at lower exposures, continued at a continuous rate, and leveled off around 80 AFU's.

At the 0.05% owf concentration level only, the initial increase in the a^* values or redness appeared to be related to the amount lost. The FWA's which increased the least amount in redness were the same FWA's which faded the most. For example, FWA's 9, 2, and 7 had the lowest initial increase in redness or Δa^* values (1.6, 2.1, and 2.4, respectively), and they also were the FWA's to become greener than the untreated cotton following exposure (Δa^* = -0.3, 0.1, and -0.2, respectively). These FWA's also exhibited the lowest initial whiteness (WI = 100.8, 106.4, and 108.4), actual concentrations (0.02% owf for FWA's 7 and 9 and 0.03% owf for FWA 2), and close to the lowest fluorescence intensity (F = 0.72, 0.79, and 0.84). FWA 4 exhibited the least amount of change in its Δa^* value after 160 AFU's (0.7) and the highest initial Δa^* value (3.9). It also had the greatest initial whiteness (WI = 124.1) and fluorescence (F = 1.00), and the lowest percentage change in whiteness and second lowest change in fluorescence intensity, although not significantly different from

FWA 3, which had the least change in fluorescence.

Even though the Δa* values did influence the total color difference values (ΔE), the blueness/yellowness coordinate (b*) was probably the most important colorimetric parameter because of its direct influence on the preceived whiteness of items. The b* value had the greatest amount of change, compared to the other chromaticity coordinates after exposure, with some samples showing an appreciable yellowing. The Δb* values ranged from -5.1 to 2.8. The b* component is positive (+) when yellow and negative (-) when blue. When the Δb* is positive, this reflects greater yellowness in the FWA-treated samples than in the unexposed untreated cotton; whereas a negative (-) Δb* value between 0 and -1.1 denotes increasing yellowness in the sample but less than the untreated cotton. Values of Δb* less than -1.1 reflect greater blueness in the FWA-treated sample.

Initially, the Δb* values ranged from -3.5 to -7.6 due to the FWA treatment. These values suggested that the treatment caused a shift in the color of the cotton from yellow (+b*) to blue (-b*). As the exposure level increased, the blueness in the samples decreased and the yellowness increased. At 10 AFU's the Δb* values ranged from -5.1 to -1.3, at 20 AFU's values ranged from -4.0 to -0.8 with just one treatment showing an increase in yellowness. Seven treatments increased in yellowness after 40 AFU's, with values ranging from -2.8 to 0.5. One sample was yellower than the unexposed untreated cotton. After 80 AFU's of xenon exposure, Δb* values ranged from -1.6 to 2.0 with all but four treatments increasing in yellowness and nine exhibiting greater yellowness than the untreated cotton. All of the

FWA-treated samples increased in yellowness after 160 AFU´s, with values ranging from -0.8 to 2.8. Twelve treatments were yellower than the unexposed untreated cotton. Overall, the fading behavior exhibited by the FWA´s for the Δa^* values were similiar to those for the Δb^* values as well with the greatest fading occurring at 10 AFU´s of exposure. Fading also tended to level off after 80 AFU´s.

The greatest changes in the b^* values after 160 AFU´s were associated with the 0.50 and 1.0% owf treatments. It is obvious that some of the FWA´s caused appreciable yellowing in the fabric rather than just a loss of the initial blueness imparted by the FWA. After 80 or 160 AFU´s FWA´s 4, 5, and 8 at the 0.50 and 1.0% owf concentrations were appreciably yellower than the unexposed untreated cotton. At these theoretical concentrations, FWA´s 5 and 8 had the greatest actual concentrations compared to the other FWA´s, whereas FWA 4 had only a moderate amount present compared to the other FWA´s. FWA´s 5 and 8 exhibited their highest initial whiteness (WI = 125.3 and 122.6, respectively) and fluorescence intensity (F = 1.05 and 1.04) at the 0.50% owf concentration, but lower values were obtained for these FWA´s at the 1.0% owf concentration (WI = 122.2 and 116.2, F = 1.04 and 0.95). This probably was attributed to fluorescence self-extinguishment at the higher FWA concentration. This is further substantiated by the initial Δa^* and Δb^* values for these FWA´s which were the highest at the 0.50% owf concentration and less at the 1.0% owf concentration. In both instances, less blueness and redness was imparted to the fabric. The ΔE values also were lower at the 1.0% owf concentration than at the 0.50% owf concentration.

In addition to FWA 4 having only a moderate actual concentration, compared to the other FWA's, it exhibited its greatest initial whiteness and fluorescence at the lowest theoretical concentration (0.05% owf) as well as the greatest increase in redness and blueness in this sample. FWA's 4, 5, and 8 exhibited the greatest percentage changes in whiteness, however, none of these FWA's experienced the greatest change in fluorescence, with the means for these FWA's falling within the means for the others. In fact, FWA 4 lost the least amount of fluorescence overall.

At the 0.05% owf concentration, FWA 9 was the only FWA to exhibit greater yellowing (although not appreciable), compared to the unexposed untreated cotton after 160 AFU's, with values ranging from −0.8 to 0.2. Although all the samples lost their blueness and increased in yellowness, they were not as yellow as the unexposed untreated control (except FWA 9 as discussed or FWA 7 which had a Δb^* value of 0). Similar to the findings reported for the Δa^* values, the initial increase in the Δb^* values correlated with the amount lost after exposure. FWA 9 had the lowest initial increase in blueness ($\Delta b^* = -3.5$) and the greatest increase in yellowness ($\Delta b^* = 0.2$) after 160 AFU's of xenon exposure. FWA 9 which had the lowest actual concentration (0.02% owf), exhibited the greatest percentage change in whiteness (−88.2%) and fluorescence (−67.8%) at the 0.05% owf concentration, and had the lowest initial whiteness (WI = 100.8) and fluorescence (F = 0.72).

Samples treated with FWA's 4 and 8 had the least amount of yellowing with $\Delta b^* = -0.8$ and -0.6, respectively. These treatments also resulted in the greatest initial whiteness (WI = 124.1 and 117.2) and fluorescence (F = 1.00 and 0.98). FWA 4 had the lowest percentage change in whiteness (-64.0%) and second to the lowest change in fluorescence intensity (-43.2%, although not significantly different from the lowest), while FWA 8 fell in between all the other FWA's.

In summary, the Δb^* values had the greatest influence on total color difference (ΔE) because of the blueness/yellowness hue shifts in the samples as a result of the FWA treatments. Blueness and yellowness are directly related to the perception of whiteness with bluish whites being considered more brilliant, cleaner, and whiter than those which have a slightly yellow cast. The Δb^* values increased as xenon exposure increased with a yellow hue being imparted to some of the samples, especially after 80 and 160 AFU's of xenon exposure. FWA's 4, 5, and 8 experienced the greatest increase in yellowness with samples becoming yellower than the unexposed untreated cotton at the 0.50 and 1.0% owf concentrations. FWA's 1, 2, and 6 experienced the least yellowing of all the treated samples. However, at the 0.05% owf concentration FWA 9 was the only FWA to exhibit more yellowing than the untreated cotton, while FWA's 4 and 8 exhibited the least amount of yellowing. The Δa^* value also influenced the color difference values, but it was not as influential as the Δb^* value. The redness initially imparted by the FWA's was lost, and the samples tended to become slightly greener as exposure increased. FWA's 7 and 9 may have exhibited more greenness than the untreated cotton, although very slight. The L^* value did not change appreciably and had little effect on the ΔE values.

Comparison of Changes in Whiteness, Fluorescence Intensity, and Chromaticity

At each xenon exposure level, the percentage change in whiteness exceeded the change in fluorescence. For example, the grand means of the 0.05% owf concentration for whiteness at 10, 20, 40, 80, and 160 AFU´s were -42.7%, -58.2%, -73.8%, -87.4%, and -96.6%, whereas the corresponding values for change in fluorescence were -27.4%, -37.6%, -49.8%, -62.0%, and -72.2%, respectively. Perhaps additional factors than just loss in fluorescence were contributing to the greater change in whiteness, such as yellowing. Lanter (60) states that fluorescence values should not be used for comparative assessment of lightfastness, since discoloration caused by decomposition products is not recorded. However, a better understanding of the changes occurring in the FWA-treated samples during light exposure can be obtained by comparing whiteness and chromaticity values. Because the higher theoretical concentrations (0.50 and 1.0% owf) often exceeded the maximum amount needed for optimum fluorescence, the following comparisons will be limited to data for the 0.05% owf theoretical concentration.

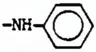
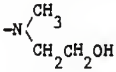
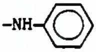
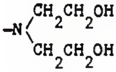
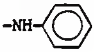
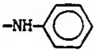
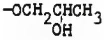
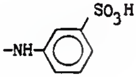
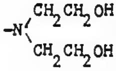
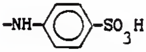
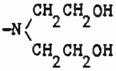
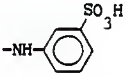
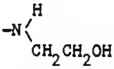
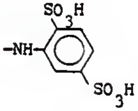
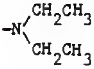
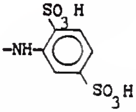
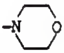
Based on the grand means for percentage change in whiteness and fluorescence after xenon exposure, FWA´s 9, 7, 2, and 6 exhibited the greatest change in both whiteness and fluorescence, whereas FWA´s 3 and 4 exhibited the least change. The values for FWA´s 1, 5, and 8 fell in between the above groups, and their rank orders differed for percentage change in whiteness (1, 5, and 8) and fluorescence (8, 5, and 1). However, there was no significant difference between the grand means for percentage change in fluorescence associated with FWA´s 8, 5, and 1; whereas the grand mean for percentage change in whiteness associated with FWA 1 was significantly higher than those for FWA's 5 and 8. Samples treated with FWA 1 may have had slightly more yellowing during exposure compared to FWA's 5 and 8. A summary of the data for the dependent variables (whiteness, fluorescence, and chromaticity) and chemical structure for the nine FWA treatments at the 0.05% owf concentration is presented in Table 46.

As previously discussed, the greatest overall percentage change in both whiteness and fluorescence during xenon exposure was observed for FWA's 9, 7, 2, and 6 (descending order). However, there appeared to be a relationship between the actual concentration of the FWA applied to the cotton samples and the subsequent loss in fluorescence or fading during xenon exposure. For example, the samples treated with FWA 9 had the lowest initial whiteness (WI = 100.8), fluorescence intensity (F = 0.72) chromaticity ($\Delta a^* = 1.6$, $\Delta b^* = -3.5$), and color difference ($\Delta E = 3.8$) value. After 160 AFU's of xenon exposure, the samples treated with FWA 9 exhibited yellowing, as reflected by the chromaticity values. This FWA exhibited the greatest increase in yellowness ($\Delta b^* = 0.2$) and decrease in redness or increase in greenness ($\Delta a^* = -0.3$), which often accompanies yellowing. As in the case of FWA 9, fading or loss in fluorescence intensity may occur more extensively in samples that initially exhibit minimal increases in fluorescence and whiteness. In addition, this relationship also may be influenced by fluorescence efficiency as well as concentration of the FWA. It is well known that concentration influences the lightfastness of dyes (7). Similarly, samples treated with FWA 7, which initially ranked the third lowest in initial whiteness (WI =

Table 46. Comparison of Actual Concentration, FWA Type, Whiteness, Fluorescence Intensity, Chromaticity, and Functional Groups at the 0.05% owf Theoretical Concentration

Actual Conc. (% owf)	FWA	Whiteness			Fluorescence		
		WI	ΔWI^*	Change in WI, %	F	ΔF^*	Change in F, %
0.05	5	114.2	33.0	−68.0	0.91	0.88	−46.0
	8	117.2	35.8	−65.6	0.98	0.95	−48.3
0.04	4	124.1	42.8	−64.0	1.00	0.98	−43.2
	3	112.8	31.4	−65.3	0.86	0.83	−42.4
	1	109.1	27.8	−69.9	0.80	0.78	−45.4
	2	106.4	25.0	−72.5	0.79	0.76	−50.3
0.03	6	113.6	32.2	−71.7	0.90	0.88	−49.1
0.02	9	100.8	19.4	−88.2	0.72	0.69	−67.8
	7	108.4	26.2	−60.5	0.84	0.82	−57.5

Table 46 cont.

Chromaticity								Functional Groups	
0 AFU's				160 AFU's					
ΔL*	Δa*	Δb*	ΔE	ΔL*	Δa*	Δb*	ΔE	X	Y
0.2	2.9	-5.8	5.6	-0.2	0.1	-0.4	0.4		 $-N(CH_3)(CH_2CH_2OH)$
0.2	3.2	-6.3	7.0	-0.2	0.2	-0.6	0.6		 $-N(CH_2CH_2OH)(CH_2CH_2OH)$
0.2	3.9	-7.4	8.4	-0.4	0.7	-0.8	1.1		$-OCH_3$
0.1	2.8	-5.6	6.2	-0.3	0.2	-0.6	0.7		 $-OCH_2CH(OH)CH_3$
0.1	2.5	-4.9	5.5	-0.2	0.0	-0.2	0.2		 $-N(CH_2CH_2OH)(CH_2CH_2OH)$
0.2	2.1	-4.4	4.9	-0.2	-0.1	-0.2	0.3		 $-N(CH_2CH_2OH)(CH_2CH_2OH)$
0.2	2.8	-5.6	6.4	-0.3	0.0	-0.2	0.4		 $-N(H)(CH_2CH_2OH)$
0.1	1.6	-3.5	3.8	-0.2	-0.3	0.2	0.4		 $-N(CH_2CH_3)(CH_2CH_3)$
0.1	2.4	-4.8	5.4	-0.2	-0.2	0.0	0.2		

108.4) and chromaticity ($\Delta a^* = 2.4$, $\Delta b^* = -4.8$, and $\Delta E = 5.4$), and the fourth lowest in initial fluorescence intensity (F = 0.84), lost all of their blueness (after 160 AFU´s) to the extent that they had the same mean b* values as the untreated control (i.e., $\Delta b^* = 0$). Interestingly, FWA´s 9 and 7 had the lowest actual concentration initially which may have resulted in a greater amount of fading or loss in fluorescence, compared to the other FWA treatments.

Chemically, both FWA 9 and 7 had disulfonated anilino groups in the X position, but differed in the Y functional group with FWA 9 containing a diethyl amino group and FWA 7 a morpholino group. Based on dyestuff literature (39), sulfonic acid groups often increase lightfastness. However, it is known that concentration can substantially influence lightfastness as well. Perhaps the low concentration levels (0.02% owf) and fluorescence imparted by FWA´s 9 and 7 had a greater influence on lightfastness than did the sulfonic acid groups, resulting in greater percentage loss of whiteness or a greater amount of FWA fading during xenon exposure when compared to the other FWA treatments

FWA´s 2 and 6, which had the third and forth highest mean percentage changes in whiteness (-72.5% and -71.7%) and fluorescence intensity (-50.3% and -49.1%) after xenon exposure, and had actual concentrations of 0.04% and 0.03% owf, respectively. FWA 2 had initial whiteness (WI = 106.4) and fluorescence (F = 0.79) values which preceded only FWA 9, while FWA 6 ranked forth in initial whiteness (WI = 113.6) and fluorescence intensity (F = 0.90). FWA 2 had a greater initial fluorescence than FWA 9 which could be attributed to the slightly higher actual concentration of FWA 2 (0.04% owf) or to the dihydroxyethyl amino groups. FWA 9 did not contain hydroxyl end groups on the ethyl amino group in the Y position, and these groups increase fluorescence intensity (91). Sulfonic acid groups, which often increase the solubility and lightfastness of dyes, have been shown to decrease fluorescence intensity (91) and could have contributed to the greater initial fluorescence and whiteness values for FWA 2, which had fewer sulfonic acid groups than FWA 9.

FWA 6 contained fewer hydroxyl groups on the ethyl amino functional group than FWA 2 which might be expected to decrease fluorescence intensity. However, the meta position of the sulfonic acid group on the anilino compound in FWA 6 may be responsible for the greater fluorescence intensity. An electron withdrawing group (i.e, $-SO_3H$) para to an electron donating group, such as in FWA 2, will decrease fluorescence. An electron withdrawing group in the meta position would also decrease fluorescence, however the effect may not be as great; while a donating group in the para position enhances fluorescence (91). The better lightfastness of FWA 6, as compared to FWA 2, may be attributed to higher initial whiteness and fluorescence intensity values and to the fewer hydroxyl groups on the FWA molecule which decrease the lightfastness of dyes (34).

As mentioned previously, FWA´s 8, 5, and 1 were not significantly different in their percentage change in fluorescence intensity (-46.3%, -46.0%, and -45.4%, respectively), and their rank differed only slightly (1, 5, and 8) for percentage change in whiteness (-69.9%, -68.0%, and -65.6%), although FWA´s 1 and 8 were significantly different from each other. FWA´s 5 and 8 had actual concentrations of 0.05% owf, while FWA 1 had a slightly lower concentration of 0.04% owf. The rank order for initial fluorescence intensity of all the FWA´s was very similar to that for initial whiteness, with the rank order of the three FWA´s being exactly the same for both (8, 5, and 1). The initial whiteness values for FWA´s 8, 5, and 1 were 117.2, 114.2, and 109.1, and the corresponding fluorescence intensity values were 0.98, 0.91, and 0.80, respectively. Because the rank orders for initial whiteness and fluorescence intensity and percentage change in fluorescence intensity were the same (8, 5, and 1), while percentage change in whiteness differed slightly (1, 5, and 8), it appeared that FWA 1 exhibited more yellowing than FWA 5 or 8. The change in chromaticity values show that FWA 1 had the greatest yellowing, as indicated by the hue shift to yellow/green, followed by FWA 5. Samples treated with FWA 8 exhibited less yellowing than FWA´s 5 or 1. Although the greater initial fluorescence intensity and whiteness of FWA´s 5 and 8 could be attributed to the higher concentrations. Compared to FWA 1, the Y functional group for FWA 8 (which had the highest initial fluorescence) was a dihydroxyethyl amino group, whereas FWA 5 contained a monohyroxyethyl amino group. The additional hydroxyl groups were probably contributing to the increase in fluorescence. No sulfonic acid groups were present on the anilino X functional group in either FWA 8 or 5, yet the anilino group on FWA 1 was monosulfonated which may account for the lower initial fluorescence intensity as well as the lower actual concentration.

The samples treated with FWA 1 had less change in fluorescence intensity (-45.4%) after xenon exposure, compared to FWA´s 5 and 8, but exhibited the greatest change in whiteness (-69.9%). FWA´s 1 and 8 had identical structures, except for the sulfonic acid group on the anilino structure in the X position of FWA 1, which may have been responsible for its lower initial fluorescence intensity but greater resistance to fading or loss of fluorescence. Even though the samples treated with FWA 1 had less change in fluorescence during light exposure, they exhibited more yellowing than did the other FWA treatments as indicated by the changes in whiteness and chromaticity. FWA 8 imparted greater initial fluorescence intensity and whiteness to the cotton fabric and retained more whiteness than did FWA´s 5 or 1, yet it exhibited a slightly greater loss in fluorescence during xenon exposure. This could be due to the replacement of one of the ethylhydroxy groups in FWA 5 with a methyl group which has been reported to increase the lightfastness of FWA´s (35). However, the change in whiteness was greater in FWA 5 which also was evident in the change in color values.

FWA´s 1 and 2 had similar chemical structures except for the location of the sulfonic acid group on the anilino group which was para for FWA 2 and meta for FWA 1. The sulfonic acid groups in the para position may have been responsible for the lower initial fluorescence and the increased fading of FWA 2 versus the location of the sulfonic acid groups in the meta position for FWA 1. An electron withdrawing group para to an electron donating group has been shown to decrease lightfastness in some dyes (34), as well as decrease fluorescence intensity (91). The greater initial fluorescence intensity and whiteness of FWA 1 also seemed to influence the amount of fading that occurred with more fading or loss of fluorescence and whitening occurring when less initial fluorescence intensity and whiteness was imparted, as in FWA 2.

FWA's 1 and 6 are also similar in structure, differing only in the Y functional group. FWA 1 has a dihydroxyethyl amino group while FWA 6 has a monohydroxyethyl amino group. It might be expected that FWA 1 would have had the greatest initial fluorescence intensity because of the greater number of hydroxyl groups and its greater actual concentration. However, FWA 6 had greater initial fluorescence and whiteness as well as greater fading of whiteness and fluorescence intensity which can not be accounted for structurally.

FWA's 3 and 4 exhibited significantly less changes in whiteness and fluorescence than did the other FWA's, although they were not significantly different from each other. FWA 4 had a greater loss in fluorescence (-43.2%) than did FWA 3 (-42.4%), whereas change in whiteness was greater in FWA 3 (-65.3%) than in FWA 4 (-64.0%). FWA 4 had greater initial whiteness (124.1) and fluorescence intensity (1.00) than did FWA 3 (112.8 and 0.86). Both of these FWA's contained oxygen in the Y functional groups as the link to the parent molecule. Alkoxy groups, especially methoxy (FWA 4), have been found to increase both fluorescence intensity and lightfastness of FWA's (22,35,42,91). This appeared to influence the initial fluorescence intensity, whiteness, and the percentage change in fluorescence and whiteness as observed in the values obtained for both FWA's.

Effect of FWA's on the Breaking Strength of the Cotton Fabric

The breaking strength (BS) means at 0.05 and 1.0% owf for each replica of the experiment are presented in Table A9, Appendix A. Each replica mean was based on five individual breaking load tests taken on the samples prior to and following 160 AFU's of xenon exposure. The overall breaking strength means, computed on the replica means, are presented in Table 47. (Note: Because of time limitations, the 0.50% owf concentration was not evaluated, and breaking load measurements were only taken before and after 160 AFU's of xenon exposure.)

Before Xenon Exposure

Percentage change in breaking strength was computed for the FWA's prior to xenon exposure to determine if the treatments appreciably affected the physical properties of the 100% cotton fabric. The following formula, based on the difference in breaking strengths (lbs) between the unexposed untreated and unexposed FWA-treated samples, was used to calculate percentage change as shown:

$$\begin{array}{c}\text{\% Change in}\\\text{Breaking Strength}\end{array} = \frac{BS_{\substack{\text{unexposed}\\\text{FWA-treated}}} - BS_{\substack{\text{unexposed}\\\text{untreated control}}}}{BS_{\substack{\text{unexposed}\\\text{untreated control}}}} \times 100$$

The mean breaking strength of the unexposed untreated controls was 56.4 lbs; the subsequent mean percentage changes therein for the replicas of the 18 FWA treatments are given in Table A10, Appendix A), and the corresponding overall means for the nine FWA's at the two

Table 47. Mean Breaking Strength Values Prior to and Following Xenon Exposure (160 AFU´s)

FWA	Concentration (% owf)	Breaking Strength, lbs Exposure (AFU´s) 0	 160
Control	0.0	56.4	47.4
1	0.05	54.9	46.2
	1.0	54.3	48.2
2	0.05	53.4	47.4
	1.0	53.4	47.6
3	0.05	53.2	48.0
	1.0	55.8	49.6
4	0.05	55.7	50.6
	1.0	54.8	48.7
5	0.05	56.2	48.0
	1.0	53.2	48.5
6	0.05	55.4	48.0
	1.0	54.6	46.9
7	0.05	54.5	44.4
	1.0	54.8	48.0
8	0.05	55.7	48.2
	1.0	55.6	50.7
9	0.05	56.0	45.1
	1.0	54.4	47.0

concentrations are given in Table 48.

Table 48. Mean Percentage Change in Breaking Strength for FWA Treated Samples Before Xenon Exposure Based on Unexposed Untreated Controls

FWA	Concentration (% owf)	Change in Breaking Strength, %
1	0.05	-2.8
	1.0	-3.7
2	0.05	-5.4
	1.0	-5.4
3	0.05	-5.6
	1.0	-1.2
4	0.05	-1.3
	1.0	-3.0
5	0.05	-0.3
	1.0	-5.6
6	0.05	-1.8
	1.0	-3.2
7	0.05	-3.4
	1.0	-3.0
8	0.05	-1.3
	1.0	-1.5
9	0.05	-0.1
	1.0	-3.6

Initially, all of the FWA treatments caused a slight to moderate decrease in breaking strength with mean percentage changes ranging from -0.3% (FWA 5, 0.05% owf) to -5.6% (FWA 3, 0.05% and FWA 5, 1.0% owf). Based on the analysis of variance test, neither independent variable or the interaction between them were significant (see Table 49). There was no significant difference among the means associated with FWA type which ranged from -1.4% (FWA 8) to -5.4 (FWA 2) (see Table 50), or between the means for concentration of 0.05 and 1.0% owf which were -2.6% and -3.4%, respectively (see Table 51).

Table 49. Analysis of Variance for Mean Percentage Change in Breaking Strength of the FWA Treated Samples Before Xenon Exposure Based on Unexposed Untreated Controls

Source of Variation	Degrees of Freedom	Sum of Squares	F-Value	PR>F
FWA	8	0.004	0.48	0.8523
Concentration	1	0.001	0.57	0.4609
FWA x Concentration	8	0.006	0.67	0.7135

FWA: 1-9
Concentration: 0.05, 1.0% owf

Table 50. Duncan´s Multiple Range Test on Mean Percentage Change in Breaking Strength for FWA Types Before Xenon Exposure Based on Unexposed Untreated Controls

FWA	Mean (%)	Grouping*
2	-5.4	A
3	-3.4	A
1	-3.2	A
7	-3.2	A
5	-3.0	A
6	-2.5	A
9	-2.2	A
4	-2.2	A
8	-1.4	A

* Means with the same letter are not significantly different at the 0.05 level.

Table 51. Duncan´s Multiple Range Test on Mean Percentage Change in Breaking Strength for FWA Concentration Before Xenon Exposure Based on Unexposed Untreated Controls

Concentration (% owf)	Mean (%)	Grouping*
1.0	-3.4	A
0.05	-2.6	A

* Means with the same letter are not significantly different at the 0.05 level.

Slight variations were observed in the effect of actual versus theoretical concentration for the FWA types within a concentration level and between theoretical concentration levels. For example, FWA 8, 5, and 6 had the highest actual concentration at the 0.05% owf theoretical concentration (actual = theoretical), but their percentage change in breaking strength means were among the lowest for all FWA treatments. Likewise, FWA 7 had the lowest actual concentration (i.e., 0.02% owf) at the 0.05% owf theoretical concentration, but exhibited more strength loss (-3.4% change) than FWA's 5, 8, 6, 1, and 4 which had actual concentrations that were twice as large (0.04 to 0.05% owf) as FWA 7 (0.02% owf).

The 1.0% owf FWA treatments caused a slightly greater loss in strength with 6 of the FWA's (i.e., FWA's 5, 1, 9, 6, 4, and 8), compared to the 0.05% owf concentration. In addition, FWA 5 had the highest actual concentration (0.66% owf) at the 1.0% owf theoretical level, and the highest change in breaking strength (-5.6%), but FWA 8 with the second highest actual concentration (0.57% owf) had next to the lowest mean change (-1.5%). FWA's 9 and 7 had the lowest actual concentration at the 1.0% theoretical level (i.e., 0.09% and 0.08% owf) but exhibited strength losses comparable to some of the other FWA types with slightly higher actual concentrations.

In summary, all of the FWA treatments (before xenon exposure) caused a slight decrease in the breaking strength, compared to the untreated controls. However, there were no significant differences in the mean percentage change in breaking strength means among the FWA types and concentrations. The FWA's differed slightly in the amount of strength loss exhibited at the two concentrations and in the actual concentration present within a theoretical concentration level.

After Xenon Exposure

Samples of the untreated and FWA-treated cotton were exposed to 160 AFU's of xenon light and then evaluated for percentage change in breaking strength to 1) determine if the FWA's accelerated phototendering and 2) evaluate the relationship between the lightfastness of the FWA and changes in breaking strength. The breaking strength values for the exposed FWA-treated samples ranged from 44.4 to 50.7 lbs with the mean for the untreated control (47.4 lbs) falling within this range (see Table 47). The percentage change in breaking strength after exposure was based on the breaking strength values of the exposed untreated control, with a loss in strength designated by a negative value, whereas a positive value indicates an increase in strength or less strength loss than the exposed untreated controls, as shown below:

$$\begin{array}{c}\text{\% Change in}\\ \text{Breaking Strength}\end{array} = \frac{BS_{\substack{\text{exposed}\\ \text{FWA-treated}}} - BS_{\substack{\text{exposed}\\ \text{untreated control}}}}{BS_{\substack{\text{exposed}\\ \text{untreated control}}}} \times 100$$

The mean percentage change in breaking strength for the FWA treatments following exposure, are presented in Table 52 and replication means are presented in Table A11, Appendix A. These values represent the combined effects of the FWA application and changes subsequent to 160 AFU´s of xenon exposure. After exposure some of the FWA´s exhibited less strength loss than the exposed untreated control, whereas while others lost more strength.

Table 52. Mean Percentage Change in Breaking Strength for FWA Treated Samples After Xenon Exposure Based on Exposed Untreated Controls

FWA	Concentration (% owf)	Change in Breaking Strength, %
1	0.05	-2.5
	1.0	+1.6
2	0.05	+0.2
	1.0	+0.2
3	0.05	+1.4
	1.0	+4.6
4	0.05	+6.8
	1.0	+2.8
5	0.05	+1.2
	1.0	+2.2
6	0.05	+1.2
	1.0	-1.0
7	0.05	-6.4
	1.0	+1.2
8	0.05	+1.6
	1.0	+7.0
9	0.05	-4.8
	1.0	-0.8

However, the majority of the FWA-treated fabrics exhibited less strength loss during xenon exposure than did the controls as indicated by the positive values, except for FWA 6 at 1.0% owf (-1.0% change), FWA 1 at 0.05% owf (-2.5% change), FWA 7 at 0.05% owf (-6.4% change), and FWA 9 at 0.05 and 1.0% owf (-4.8% and -0.8% change). Only the values for FWA's 7 and 9 at the 0.05% concentration were considered appreciably greater strength losses. However, changes of less than 10% often are considered as minimal in the textile industry when evaluating the effects of dyes, finishes, processing variables, environmental factors, etc. on substrates. Those FWA types and concentration levels that resulted in appreciably less strength loss (> +2%) during xenon exposure compared to the untreated controls include: FWA's 8 at 1.0% owf (+7.0% change), FWA 4 at 0.05 and 1.0% owf (+6.8% and +2.8% change), FWA 3 at 1.0% owf (+4.6% change), and FWA 5 at 1.0% owf (+2.2% change).

Both FWA type and concentration had a significant effect on the mean percentage changes in breaking strength (see Table 53), thus Duncan's Multiple Range Tests were performed on the grand means for these independent variables (see Table 54 and 55). The grand means for FWA's 4 (+4.8%) and 8 (+4.3%) were significantly higher than those associated with the other FWA types, whereas FWA's 7 (-2.5%) and 8 (-2.8%) exhibited significantly lower means which were attributed primarily to strength losses at the 0.05% owf concentration.

Table 53. Analysis of Variance for Mean Percentage Change in Breaking Strength of the FWA Treated Samples After Xenon Exposure Based on Exposed Untreated Controls

Source of Variation	Degrees of Freedom	Sum of Squares	F-Value	PR>F
FWA	8	0.02	20.68	0.0001*
Concentration	1	0.01	28.40	0.0001*
FWA x Conc.	8	0.01	9.62	0.0001*

* Significant at the 0.01 level.

FWA: 1-9
Concentration: 0.05, 1.0% owf

Table 54. Duncan's Multiple Range Test on Mean Percentage Change in Breaking Strength for FWA Types After Xenon Exposure Based on Exposed Untreated Controls

FWA	Mean (%)	Grouping*
4	+4.8	A
8	+4.3	A
3	+3.0	A B
5	+1.7	B C
2	+0.2	C D
6	+0.1	C D
1	-0.4	D
7	-2.5	E
9	-2.8	E

* Means with the same letter are not significantly different at the 0.05 level

Table 55. Duncan´s Multiple Range Test on Percentage Change in Breaking Strength for FWA Concentration After Xenon Exposure Based on Exposed Untreated Controls

Concentration (% owf)	Mean (%)	Grouping*
1.0	+2.0	A
0.05	-0.2	B

* Means with the same letter are not significantly different at the 0.05 level.

It is interesting to note that all of the FWA´s which lost more strength than the exposed controls (1, 7, and 9) had sulfonated anilino groups in the X position, with FWA´s 7 and 9 being disulfonated (see Table 2). The FWA´s which had less strength loss than the exposed controls (4, 8, 3, 5, 2, and 6, in order of decreasing magnitude) contained either an unsulfonated or mono-sulfonated anilino group in the X position.

Among those FWA treatments which exhibited less change in breaking strength than the exposed untreated controls, the higher concentration usually, but not always (i.e., FWA 4), had even less strength loss than did the 0.05% owf treatments. This also was reflected in the grand means for the 0.05 and the 1.0% owf concentrations which were -0.2% and +2.0%, respectively. However, it was noted that at the highest concentration (1.0% owf), some of the FWA treatments increased the stiffness of the fabric and appeared to "glue" the yarns together.

As previously discussed, there was an inverse relationship between actual versus theoretical concentration and strength losses during exposure. Compared to the exposed untreated controls, the FWA treatments which had the lowest actual concentrations (FWA´s 7 and 9) had more strength loss after exposure, whereas the FWA treatments which had the highest actual concentrations (FWA 4) had less strength loss than the untreated controls.

The interaction between FWA type and concentration following 160 AFU´s of xenon exposure was significant (see Table 56 and Figure 6). Because some FWA´s exhibited an increase in strength and others a decrease in strength compared to the exposed untreated control, this interaction was significant. FWA´s 7 and 9 lost the greatest amount of strength compared to the control, however, their actual concentration on the fabric, as said before, were also the lowest.

Table 56. Mean Percentage Change in Breaking Strength for FWA Types at Each Concentration After Xenon Exposure Based on Exposed Untreated Controls

	Change in Breaking Strength, %	
	Concentration (% owf)	
FWA	0.05	1.0
1	-2.5	+1.6
2	+0.2	+0.2
3	+1.4	+4.6
4	+6.8	+2.8
5	+1.2	+2.2
6	+1.2	-1.0
7	-6.4	+1.2
8	+1.6	+7.0
9	-4.8	-0.8

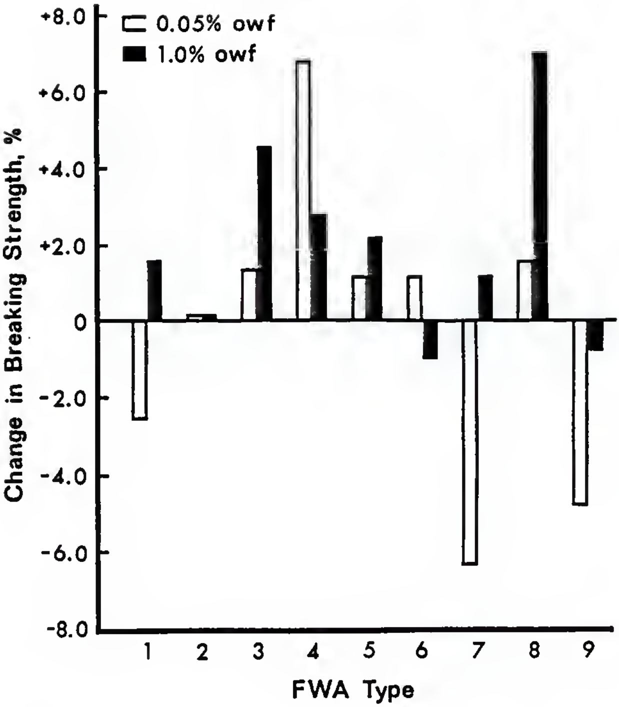


Figure 6. Mean Change in Breaking Strength for FWA Types at Each Concentration.

In summary, after xenon exposure FWA´S 1, 7, and 9 exhibited greater strength loss than the exposed untreated control, while all of the other FWA treatments lost less strength than the exposed untreated control. FWA treatments at 0.05% owf lost more strength, whereas the 1.0% owf treatments overall, exhibited less strength loss than the exposed untreated control. However, it appeared that the FWA treatments which had the lowest actual concentration at each theoretical concentration level had more strength loss than those with the highest actual concentrations. The interaction between FWA type and concentration also was significant because some FWA´s exhibited greater strength loss than the exposed untreated control while others exhitited less strength loss at the same concentration. The change in strength values ranged from -6.4% to +7.0%. These values were below the 10% level which is often used as a bench mark by the textile industry for evaluating the effects of dyes and finishes on the strength of substrates.

SUMMARY AND CONCLUSIONS

FWA's are compounds applied to textiles to improve their apparent whiteness. They function by absorbing invisible ultraviolet radiation present in both natural and artificial light sources, converting it to visible blue light. The inherent yellow color of the textile is decreased due to an increase in the amount of blue light reflected from the fabric, actually imparting a subtle blue hue to the fabric. Fabric brightness also is improved because the total amount of light reflected from the fabric in the visible region of the electromagnetic spectrum is increased.

However, due to the higher energy associated with ultraviolet radiation, as compared to visible radiation, there is greater potential for fading and fiber degradation when the absorption of ultraviolet radiation by textile substrates is increased. This study investigated the relationship between the lightfastness properties and chemical structure of FWA's and their potential for causing fiber degradation.

Nine FWA's of the triazinylamino stilbene type, commonly applied in textile finishing and from laundry detergents, were chosen for evaluation. Their selection was based on commercial availability, chemical structure, and ease of application. The FWA's were applied by exhaustion methods to 100% cotton fabric at 0.05, 0.50, and 1.0% owf theoretical concentrations. The samples were exposed to 10, 20, 40, 80, and 160 AFU's of xenon light and evaluated for lightfastness by evaluating the changes in whiteness, fluorescence intensity, and chromaticity. Samples treated at theoretical concentrations of 0.05

and 1.0% owf and exposed to 160 AFU´s of xenon light were evaluated for changes in breaking strength to assess the effects of FWA´s on fiber degradation.

Although the FWA´s were applied at three theoretical concentrations, 0.05, 0.50, and 1.0% owf, the actual amount of each FWA exhausting from the dyebaths was not the same. At the lowest theoretical concentration (0.05% owf), the actual concentration of each FWA on the fabric varied from 0.02 to 0.05% owf. As the theoretical concentration increased, the range of the actual concentration on the fabric became wider. At the 0.50% owf theoretical concentration, the actual concentration of each FWA on the fabric ranged from 0.07 to 0.42% owf, and at 1.0% owf the actual concentrations ranged from 0.08 to 0.66% owf.

The chemical structure of the FWA´s did influence the amount that exhausted from the dyebath. Generally, as the number of water solubilizing sulfonic acid groups (SO_3 H) on the FWA molecule increased, the amount exhausting onto the fabric decreased. Of the FWA´s which did not contain sulfonic acid groups on the anilino functional group in the X position (3, 4, 5, and 8), those having an oxygen linkage to the parent molecule in the Y position (3 and 4) had lower exhaustion. Also as the number of hydroxyl (OH) end groups on the functional group in the Y position increased, the amount of FWA exhausting increased.

The initial application of the FWA to the cotton fabric increased the whiteness and fluorescence intensity of the cotton samples, as well as blueness and redness associated with the chromaticity values.

However, at the higher application levels (0.50 and 1.0% owf) these values did not always increase as the theoretical concentration of FWA on the fabric increased. This was due to self-extinguishment of the fluorescence and whiteness at the higher theoretical concentrations of some of the FWA´s. The point at which self-extinguishment occurred was not the same for each FWA and depended on its fluorescence properties. Self-extinguishment of fluorescence occurs due to the concentration of the FWA being too high, exceeding the amount necessary for increased whitening. The inherent yellow color of the FWA itself may become apparent causing the emitted blue fluorescence to be reabsorbed by the textile. However, self-extinguishment of the fluorescence may still occur even if the FWA concentration is lower than that which would cause yellowing. The FWA may absorb all of the available UV radiation, converting it to visible blue light, but for further increases in fluoresence intensity and whiteness to occur, the amount of UV radiation available to the FWA by the light source must be increased.

Because of the problems associated with self-extingusihment of the fluorescence for some of the FWA´s and the wide range of actual concentrations present at the higher theoretical concentrations, interpretation of the data focused on the lowest theoretical concentration level. However, even at the 0.05% owf concentration it was still difficult to determine if changes in whiteness, fluorescence, and chromaticity, both upon application of the FWA initially or following xenon exposure, were due to the differences in the actual concentration present or the chemical structure of the

FWA´s.

Generally, at the 0.05% owf theoretical concentration level, the FWA´s which had the highest actual concentration also had the greatest whiteness index and fluorescence intensity values. Those FWA´s containing sulfonic acid groups (SO_3H) on the anilino structure in the X position (FWA´s 1, 2, 6, 7, and 9) had lower whiteness index and fluorescence intensity values, but also had lower actual concentrations present, than those without any sulfonic acid groups on the anilino structure. Of the FWA´s which contained one sulfonic acid group on the anilino structure in the X position (FWA´s 1, 2, and 6), slightly higher whiteness and fluorescence intensity values were obtained when the group was in the meta position on the benzene ring, compared to the para position. Previous research has shown that electron withdrawing groups (such as the SO_3H group) and electron donating groups on a benzene ring in the para positions decreases fluorescence intensity (91) and may decrease it more than one in a meta position.

At the 0.50% owf theoretical concentration, all of the FWA´s increased the whiteness and fluorescence intensity of the cotton fabric, except for FWA 4 which contained a methoxy group in the Y position on the parent molecule. The methoxy group appeared to increase fluorescence intensity even when present at lower actual concentrations compared to the other FWA´s. Previous research has shown that methoxy groups do increase fluorescence intensity (42). The highest actual concentrations at this application level ranged from 0.21 to 0.42% owf (FWA´s 1, 2, 3, 5, and 8), but similar whiteness and fluorescence intensity values were observed for all of the FWA´s within this range. Those FWA´s which had the lowest values at the 0.05% owf application level (FWA´s 6, 7, and 9) exhibited the greatest increase in whiteness and fluorescence intensity at this application level. FWA´s 6 and 7 also had considerably less actual concentration present (0.07 and 0.11% owf, respectively) than the other FWA´s, yet their whiteness and fluorescence intensity values were very similar to the other FWA´s.

FWA 9 had its highest whiteness and fluorescence intensity values at the 1.0% owf application level, an appreciable increase over the 0.50% owf level. FWA´s 2 and 7 also exhibited a slight increase in whiteness and fluorescence intensity at this level. FWA´s 1 and 6 did not change appreciably, while FWA´s 3, 4, 5, and 8 showed a decrease in both values. FWA´s 5 and 8 had considerably higher actual concentrations (0.66 and 0.57% owf, repectively) than any of the other FWA´s which may account for the decrease in their whiteness and fluorescence intensity values, while FWA´s 3 and 4 both contained an oxygen linkage to the parent molecule in the Y position. The presence of the oxygen linkage increased the initial fluorescence intensity and whiteness at lower application levels.

The chromaticity values were correlated with the whiteness values for each FWA at the three application levels. The samples increased in blueness and redness due to the FWA treatments. As the whiteness decreased at the higher application levels, the chromaticity values reflected this, decreasing in blueness and redness and increasing in yellowness and greeness. The lightness of the fabric may have increased just slightly due to application of the FWA. The total color difference (ΔE) of the cotton due to the FWA treatments ranged from 3.8 to 8.8, which would be considered "noticeably" and "considerably" changed on the AATCC Gray Scale for Color Change.

After xenon exposure the treated samples were evaluated for percentage changes in the initial whiteness and relative fluorescence intensity, as well as changes in chromaticity. The changes in whiteness exceeded the changes in fluorescence intensity at every xenon exposure level. This is because colored decomposition products caused by the xenon exposure were not recorded in the fluorescence intensity values, but were included in the whiteness values.

At the higher theoretical concentration levels (0.50 and 1.0% owf), self-extinguishment of the initial fluorescence for some FWA´s and the wide range of actual concentrations present on the fabric at each theoretical concentration level made comparison of the lightfastness of the FWA´s difficult and did not always agree with the results obtained at the 0.05% owf theoretical concentration. For example, at the lowest concentration level (0.05% owf) a relationship among the actual concentration of FWA applied, the initial whiteness and fluorescence intensity imparted to the cotton, and the subsequent loss in whiteness and fluorescence existed, whereas at the higher concentration levels this relationship was not apparent. Therefore, emphasis was placed on the results for the lowest theoretical concentration level.

The loss in whiteness and fluorescence intensity increased with increasing increments of xenon exposure up to 80 AFU´s and then began to level off. An appreciable amount of fading occurred after only 10 and 20 AFU´s of xenon exposure. At 80 and 160 AFU´s the loss of whiteness exceeded 100%, indicating that something other than just loss of fluorescence was occurring, such as yellowng. This also was apparent in the chromaticity values. At the 0.05% owf concentration only, all of the FWA´s (except FWA 4) lost more than 50% of their initial whiteness after 20 AFU´s. After 160 AFU´s, most of the FWA´s had faded completely and retained less than 10% of their original increase in whiteness.

Fabrics treated with the 0.05% owf concentration level had the lowest percentage change in whiteness, whereas those treated at the 1.0% owf concentration had the lowest change in fluorescence intensity. The greatest change in whiteness was associated with the 1.0% owf concentration, although the values were not significantly different from those for the 0.50% owf concentration. Change in fluorescence intensity was greatest at the 0.50% owf concentration, though not significantly different from the 0.05% owf concentration. The difference between the fading characteristics for whiteness and fluorescence intensity was probably due to self-extinguishment of the fluorescence and yellowing caused by xenon exposure at higher concentration levels, which was reflected in the whiteness readings but not the fluorescence values. However, at the 0.05% owf concentration only, many of these confounding problems did not exist, and the changes in whiteness and fluorescence intensity for the individual FWA´s closely agreed. At the 0.05% owf concentration, FWA´s 9, 7, 2, and 6 exhibited the greatest fading, whereas FWA´s 3 and 4 exhibited the least change. FWA´s 1, 5, and 8 fell in between the above groups, differing in their rank order for change in whiteness and fluorescence intensity.

A general relationship appeared to exist between the actual concentration of FWA applied, initial whiteness and fluorescence intensity, and the subsequent fading in the samples treated at the 0.05% owf concentration level. The FWA´s with the lowest actual concentrations exhibited the lowest initial whiteness and fluorescence intensity value, and had the greatest change in whiteness and fluorescence. Concentration is known to influence the lightfastness of dyes in the same way (7). However, the FWA´s present in the highest actual concentrations at the 0.05% owf theoretical concentration level (FWA´s 5 and 8) did not exhibit the best lightfastness. This was most likely due to chemical structure differences which influenced the initial whiteness and fluorescence intensity imparted to the fabric.

FWA´s 7 and 9, which exhibited the lowest lightfastness, contained disulfonated anilino groups in the X position on the FWA molecule. The presence of the sulfonic acid groups accounts for the lower actual concentration of FWA on the fabric (0.02% owf) and may also have been responsible for the lower initial whiteness and fluorescence intensity values since sulfonic acid groups are known to decrease fluorescence intensity (91). Previous studies also have shown that these groups increase the lightfastness of FWA´s (39), but perhaps the lower actual concentration and initial whiteness and fluorescence intensity imparted, compared to the other FWA´s, had a greater influence on the lightfastness than the ability of the groups to increase lightfastness. The Y functional groups also differed between FWA's 7 and 9 which may be responsible for the difference in their initial whiteness and fluorescence intensity values and subsequent changes in these values following xenon exposure.

FWA's 2 and 6 had slightly better lightfastness than FWA's 7 or 9. Both FWA's contained monosulfonated anilino groups in the X position which increased the exhaustion and possibly the lightfastness as compared to the disulfonated anilino groups on FWA's 7 or 9. The initial whiteness and fluorescence values for FWA 2 were slightly lower than FWA 7, while FWA 6 had the highest initial values of all four FWA's. The increased lightfastness of FWA's 2 and 6, compared to FWA's 7 and 9, may be attributed to the higher actual concentration of the FWA (0.04 and 0.03% owf, respectively) and, in the case of FWA 6, to the higher initial whiteness and fluorescence intensity. However, the actual concentration of FWA 2 was higher than that for FWA 6, and FWA 2 had lower initial values and poorer lightfastness. The location of the sulfonic acid group on the anilino structure for FWA 2 and 6 differed, with FWA 2 containing the sulfonic acid group in the para position and FWA 6 in the meta position. This could account for the difference in the initial values for the FWA's, with a sulfonic acid electron withdrawing group in the para position decreasing fluorescence intensity more than one in a meta position as reported by previous researchers (91).

Both FWA's 2 and 6 also contained hydroxyl groups (OH) on the ethylamino functional group with FWA 6 containing fewer than FWA 2.

Hydroxyl groups are responsible for decreasing the lightfastness of dyes (34) and may have been responsible for the poorer lightfastness of FWA 2 which had more hydroxyl groups compared to FWA 6. Hydroxyl groups are also known to increase fluorescence intensity (91). However, this did not appear to be the case since even at a higher actual concentration, FWA 2 exhibited lower intial fluorescence intensity.

FWA´s 8, 5, and 1 exhibited better lightfastness than FWA´s 2, 6, 7, and 9. Although their rank order for loss of fluorescence intensity (8, 5, and 1) and whiteness (1, 5, and 8) were not exactly the same, they were very close. FWA´s 5 and 8 had higher actual concentrations present (0.05% owf) than FWA 1 (0.04% owf). The rank order for the initial whiteness and fluorescence intensity imparted by thesw FWA´s were the same (8, 5, and 1). FWA 8 had the highest initial values and the greatest loss in fluorescence, but the smallest loss in whiteness, whereas FWA 1 had the lowest initial values, the lowest loss of fluorescence intensity, but the greatest change in whiteness. It appeared that FWA 1 exhibited more yellowing than FWA´s 5 and 8. The chromaticity values also showed that FWA 1 had the greatest yellowing, followed by FWA´s 5 and 8. The higher initial whiteness and fluorescence intensity values for FWA´s 5 and 8 could be attributed to the higher concentration present. FWA 1 contained a monosulfonated anilino group, whereas FWA´s 5 and 8 contained no sulfonic acid groups on the anilino structure. The sulfonic acid groups, were responsible for less FWA exhausting onto the fabric and a decrease in fluorescence intensity (91). However, sulfonic acid groups have been shown to increase the lightfastness of dyes (39) which could be responsible for FWA 1 exhibiting the least change in fluorescence intensity, although greater yellowing did occur. The greater initial whiteness and fluorescence intensity values for FWA´s 5 and 8 also could be attributed to the Y functional groups. FWA 8 contained two hydroxyl groups, which are known to increase fluorescence intensity (91). FWA 1 also contained two hydroxyl groups but the effect of increasing fluorescence could have been offset by both the sulfonic acid groups in the X position decreasing fluorescence intensity and the lower actual concentration present.

FWA´s 3 and 4 had significantly better lightfastness than the other FWA types evaluated in this study. The actual concentration of these FWA´s were identical (0.04% owf), and were only exceeded by FWA´s 5 and 8 (0.05% owf). FWA 4 had the highest initial whiteness and fluorescence intensity values of all the FWA´s, while FWA 3 had values which were lower than FWA´s 4, 5, 6, and 8. Both FWA´s 3 and 4 contained oxygen as the linkage of the Y functional groups to the parent molecule. Alkoxy groups, especially methoxy groups (FWA 4), have been shown to increase both fluorescence intensity and lightfastness of FWA´s (22,35,42,91). The oxygen appeared to be responsible for the increase in fluorescence intensity of FWA 4 initially, and improved the lightfastness of both FWA´s.

Fiber degradation of the cotton due to the presence of the FWA at 0.05 and 1.0% owf concentrations was evaluated before and after 160 AFU´s of xenon exposure. All of the FWA treatments initially caused a slight decrease in the strength of the cotton fabric. However, there was no significant difference among the values associated with specific FWA types or concentration levels.

After 160 AFU's of xenon exposure, FWA's 1, 7, and 9 exhibited greater strength loss overall than the unexposed untreated control, while all of the other FWA treatments exhibited less strength loss than the control. FWA's 7 and 9 had appreciably lower actual concentrations present on the cotton at both theoretical concentrations than the other FWA's, while FWA 1 had a moderate amount. FWA's 7 and 9 contained disulfonated anilino groups in the X position on the parent molecule. Whether the strength loss was due to the low concentration present or the functional groups on the FWA molecule is difficult to determine, since the sulfonic acid groups are water solubilizing and decrease exhaustion of the FWA on the fabric. FWA 1 contained a monosulfonated anilino group in the X position which accounts for its slightly higher actual concentration than FWA's 7 or 9. FWA's 3, 4, 5, and 8 had appreciably greater strength than the unexposed untreated control after exposure. None of these FWA's contained sulfonic acid groups on the anilino functional group in the X position. FWA's 5 and 8 had the highest actual concentrations, while FWA's 3 and 4 had moderate amounts, with several FWA's being higher. FWA's 2 and 6 had just slightly greater strength than the control after exposure, although appreciably less than FWA's 3, 4, 5, and 8. Both FWA's 2 and 6 contained monosulfonated anilino groups, but the concentration of FWA 2 exceeded that observed for FWA's 3 and 4. It appeared that the presence of the sulfonic acid groups on the FWA molecule increased fiber degradation. Cotton is susceptible to acid damage which may have occurred with the FWA's which contain sulfonic acid groups. The actual concentration of FWA on the fabric also appeared to be a factor, with greater fiber degradation occurring in samples which had lower actual concentrations. However, this was not true for FWA's 3 and 4, which had both lower actual concentration of FWA present and less fiber degradation, compared to FWA 2. FWA's 3 and 4 both contained oxygen in the Y position as the link to the parent molecule, while all the other FWA's contained nitrogen.

The 1.0% owf concentration exhibited less strength loss, which could be due to the FWA protecting the fiber from the harmful UV radiation. However, it should be noted that some FWA treatments at this concentration increased the stiffness of the fabric and appeared to "glue" the yarns in the fabric together which also would appear as less of a strength loss than the unexposed untreated control. After xenon exposure, none of the FWA treatments caused a reduction in breaking strength which exceeded 10%, which often is used as a benchmark for evaluating the effects of dyes and finishes on the strength of textile substrates.

Overall, there appeared to be no distinct relationship between lightfastness of the FWA's and the extent of photodegradation which occurred in the treated fabrics. This may be attributed to the many confounding factors which influenced both values, such as actual versus theoretical concentration, self-extinguishment of the fluorescence at higher concentrations, chemical structure differences, and the effect of the FWA treatments "glueing" the yarns in the fabric together. However, at the 0.05% owf concentration, the changes in whiteness and relative fluorescence intensity were closely associated with changes in breaking strength, although their rank orders were not exactly the same.

RECOMMENDATIONS FOR FURTHER STUDY

This study investigated the lightfastness of triazinylamino stilbene FWA´s and their potential for inducing fiber degradation in cotton. The FWA´s selected for evaluation differed in their auxochromic and chromophoric functional groups present on the parent structure. Additional research is needed in this area such as evaluating lightfastness and fiber degradation when the same amount of each FWA is exhausted onto the fabric. When different amounts of each FWA are present on the fabric, such as in this study, it is difficult to determine if the changes in the dependent variables are due to the FWA chemical structure, amount of FWA present, or a combination of the two. It also is necessary to apply the FWA at concentrations below which self-extinguishment of fluorescence and whiteness occurs.

Additional FWA chemical structures need to be evaluated to develop general trends in fading and fiber degradation caused by certain functional groups. Although this study made a good attempt at this task and investigated those FWA´s most widely used, there are more FWA structures available.

This study reported that the greatest fading or change in whiteness and fluorescence occurred at the lower xenon exposure levels (i.e., 10 an 20 AFU´s), and it is these lower levels which distinguish the fading properties of the FWA´s. Future studies may wish to evaluate the FWA´s in smaller increments of xenon exposure (i.e., 5, 10, 15, 20, etc. AFU´s).

The problem of fiber degradation needs to be assessed by solubility and staining techniques to determine the type of fiber changes induced by FWA´s. Additionally, by removing the FWA (by suitable methods) prior to breaking strength tests, one might find results that differ from those obtained in this study. As reported, the higher concentrations of some FWA´s caused the fabric to stiffen after xenon exposure and the yarns tended to be glued together which influenced the breaking strength values. However, the extraction process also may influence fiber strength.

In addition to cotton, FWA´s are applied to other fiber types. Hence, other FWA and fiber type combinations need to be evaluated. Although this study investigated surface application techniques, not all FWA´s on all fiber types are applied in this manner, and those FWA´s applied by alternative methods need to be studied further.

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Appendix A

Replica Means

Table A1. Replica Means for Whiteness Index (WI) Values at each Xenon Exposure Level

			Whiteness Index, WI					
			Exposure (AFU's)					
FWA	Conc. (% owf)	Rep	0	10	20	40	80	160
Control	0.0	1	81.2	81.0	81.8	82.4	81.6	81.8
		2	81.2	82.2	82.1	81.5	81.6	81.3
1	0.05	1	108.6	97.4	93.8	88.6	84.0	83.6
		2	109.6	99.0	93.7	89.0	86.4	80.6
	0.50	1	124.7	108.6	103.4	96.2	87.4	86.4
		2	125.4	109.8	101.2	95.1	81.8	77.0
	1.0	1	126.0	109.5	104.0	96.4	86.5	86.5
		2	125.0	109.6	101.4	96.6	90.2	80.2
2	0.05	1	105.1	94.4	91.3	87.2	83.4	82.6
		2	107.6	96.8	92.2	87.9	85.2	80.8
	0.50	1	121.0	107.6	101.8	91.9	86.6	86.1
		2	124.6	108.8	101.8	94.8	79.3	76.8
	1.0	1	123.8	107.8	103.3	94.7	85.6	85.6
		2	123.8	108.9	101.2	94.2	89.0	79.4
3	0.05	1	111.4	99.6	95.2	91.4	86.6	85.3
		2	114.2	102.9	97.6	92.3	88.0	83.0
	0.50	1	122.5	106.6	99.8	91.6	82.6	82.0
		2	122.2	107.4	99.2	92.0	73.8	74.8
	1.0	1	121.1	104.3	97.6	91.0	81.5	79.2
		2	120.6	103.6	94.8	87.9	83.0	76.2
4	0.05	1	122.8	108.4	102.2	96.2	88.6	86.2
		2	125.4	111.4	103.7	96.4	90.2	83.6
	0.50	1	121.4	104.2	96.7	86.2	75.2	71.9
		2	116.0	99.2	89.8	80.8	63.0	61.0
	1.0	1	116.8	101.2	93.4	84.4	73.2	66.8
		2	110.0	93.2	85.8	78.2	71.6	60.9
5	0.05	1	113.2	100.0	96.2	91.0	85.4	84.4
		2	115.2	102.6	97.2	92.1	87.0	82.4
	0.50	1	125.8	106.8	96.2	87.4	76.0	76.1
		2	124.8	102.9	93.5	86.3	64.6	67.4
	1.0	1	123.6	103.8	95.6	82.2	69.4	71.0
		2	120.9	98.4	87.0	79.0	72.0	64.6

Table A1 cont.

FWA	Conc. (% owf)	Rep	Whiteness Index, WI					
			Exposure (AFU's)					
			0	10	20	40	80	160
6	0.05	1	112.6	99.0	94.6	89.2	84.1	82.8
		2	114.6	101.5	95.8	90.8	85.4	80.9
	0.50	1	123.6	108.2	101.8	92.6	83.6	84.1
		2	125.8	110.2	101.0	94.0	74.9	77.2
	1.0	1	124.6	108.8	102.0	93.0	84.2	82.4
		2	124.6	108.9	100.9	93.6	87.0	79.2
7	0.05	1	107.2	93.6	90.2	85.6	82.0	81.2
		2	109.6	95.0	89.4	85.8	83.0	79.6
	0.50	1	122.9	105.7	99.0	91.0	82.2	83.6
		2	123.8	105.8	98.4	92.2	79.3	76.8
	1.0	1	125.0	106.8	100.4	92.6	85.6	83.2
		2	125.4	106.8	98.8	92.6	87.1	79.6
8	0.05	1	116.2	103.0	98.2	92.6	86.8	85.4
		2	118.0	105.1	99.0	93.7	89.8	82.6
	0.50	1	124.0	105.2	98.8	87.2	74.8	74.6
		2	121.2	101.2	89.7	83.2	68.6	62.6
	1.0	1	117.8	98.6	92.0	81.2	68.2	68.2
		2	114.5	92.4	80.6	73.5	70.0	63.2
9	0.05	1	99.7	87.7	84.8	82.3	80.6	80.6
		2	101.8	89.2	85.7	83.4	82.0	79.6
	0.50	1	116.1	98.1	92.5	85.5	80.5	80.9
		2	117.4	99.2	92.4	87.0	78.6	77.8
	1.0	1	119.6	101.2	94.9	86.6	80.8	80.7
		2	121.2	102.0	93.7	88.2	84.0	77.5

Table A2. Replica Meane for Change in Whiteness Index ($\Delta WI'$) Due to FWA Treatments on 100% Cotton Fabric

FWA	Rep	Change in Whitenees Index, $\Delta WI'$		
		Concentration (% owf)		
		0.05	0.50	1.0
1	1	27.2	43.4	44.8
	2	28.4	44.0	43.7
2	1	23.8	39.8	42.6
	2	26.4	43.3	42.6
3	1	30.0	41.2	39.8
	2	33.0	40.8	39.4
4	1	41.6	40.0	35.5
	2	44.1	34.8	28.8
5	1	32.0	44.4	42.3
	2	33.9	43.5	39.6
6	1	31.2	42.4	43.3
	2	33.2	44.6	43.3
7	1	26.0	41.6	43.8
	2	28.4	42.5	44.0
8	1	35.0	42.8	36.6
	2	36.7	40.0	33.2
9	1	18.4	34.8	38.3
	2	20.5	36.0	40.0

Table A3. Replica Means for Relative Fluorescence Intensity (F) Values at Each Xenon Exposure Level

FWA	Conc. (% owf)	Rep	Relative Fluorescence Intensity, F					
			Exposure (AFU's)					
			0	10	20	40	80	160
Control	0.0	1	0.03	0.02	0.02	0.02	0.02	0.02
		2	0.02	0.02	0.02	0.02	0.02	0.02
1	0.05	1	0.78	0.58	0.53	0.46	0.32	0.26
		2	0.82	0.65	0.62	0.47	0.38	0.24
	0.50	1	1.01	0.76	0.67	0.58	0.45	0.43
		2	1.08	0.80	0.70	0.58	0.45	0.29
	1.0	1	1.04	0.74	0.66	0.60	0.46	0.44
		2	1.02	0.78	0.71	0.59	0.54	0.40
2	0.05	1	0.72	0.54	0.47	0.39	0.28	0.23
		2	0.86	0.62	0.56	0.44	0.32	0.20
	0.50	1	0.96	0.76	0.62	0.50	0.43	0.40
		2	1.06	0.86	0.71	0.59	0.42	0.25
	1.0	1	1.00	0.74	0.66	0.56	0.44	0.42
		2	1.02	0.75	0.68	0.58	0.52	0.37
3	0.05	1	0.78	0.60	0.52	0.46	0.38	0.33
		2	0.94	0.80	0.66	0.52	0.44	0.33
	0.50	1	0.91	0.68	0.58	0.52	0.40	0.40
		2	1.04	0.76	0.66	0.55	0.34	0.34
	1.0	1	0.94	0.68	0.56	0.52	0.44	0.40
		2	0.95	0.70	0.63	0.54	0.46	0.38
4	0.05	1	0.94	0.73	0.60	0.57	0.46	0.40
		2	1.07	0.84	0.70	0.58	0.52	0.41
	0.50	1	0.95	0.70	0.58	0.52	0.42	0.40
		2	0.90	0.70	0.58	0.50	0.36	0.32
	1.0	1	0.89	0.65	0.56	0.52	0.41	0.38
		2	0.80	0.64	0.56	0.50	0.44	0.37
5	0.05	1	0.87	0.66	0.58	0.49	0.36	0.32
		2	0.95	0.72	0.64	0.52	0.42	0.32
	0.50	1	1.02	0.71	0.58	0.55	0.41	0.41
		2	1.08	0.75	0.64	0.54	0.34	0.34
	1.0	1	0.99	0.71	0.62	0.53	0.42	0.42
		2	1.08	0.71	0.61	0.52	0.46	0.38

Table A3 cont.

FWA	Conc. (% owf)	Rep	Relative Fluorescence Intensity, F					
			Exposure (AFU's)					
			0	10	20	40	80	160
6	0.05	1	0.83	0.62	0.55	0.43	0.36	0.28
		2	0.98	0.70	0.60	0.52	0.39	0.26
	0.50	1	1.02	0.76	0.64	0.52	0.40	0.42
		2	1.11	0.87	0.68	0.61	0.30	0.32
	1.0	1	1.02	0.76	0.63	0.54	0.44	0.40
		2	1.05	0.78	0.68	0.58	0.50	0.38
7	0.05	1	0.79	0.54	0.50	0.37	0.24	0.17
		2	0.90	0.60	0.52	0.38	0.28	0.14
	0.50	1	1.02	0.68	0.59	0.51	0.33	0.36
		2	1.13	0.76	0.64	0.56	0.32	0.18
	1.0	1	1.06	0.71	0.63	0.53	0.42	0.36
		2	1.14	0.78	0.66	0.54	0.46	0.30
8	0.05	1	0.90	0.66	0.60	0.53	0.42	0.36
		2	1.06	0.78	0.66	0.56	0.47	0.32
	0.50	1	1.02	0.76	0.63	0.55	0.42	0.42
		2	1.06	0.74	0.60	0.56	0.42	0.31
	1.0	1	0.92	0.76	0.60	0.54	0.42	0.42
		2	0.98	0.67	0.56	0.50	0.46	0.39
9	0.05	1	0.68	0.41	0.32	0.20	0.12	0.09
		2	0.76	0.48	0.38	0.26	0.17	0.08
	0.50	1	0.90	0.62	0.49	0.38	0.23	0.22
		2	1.04	0.68	0.56	0.45	0.18	0.06
	1.0	1	1.02	0.68	0.53	0.42	0.29	0.28
		2	1.04	0.68	0.58	0.48	0.38	0.19

Table A4. Replica Means for Change in Relative Fluorescence Intensity ($\Delta F'$) Due to FWA Treatments on 100% Cotton Fabric

FWA	Rep	Change in Relative Fluorescence Intensity, $\Delta F'$		
		Concentration (% owf)		
		0.05	0.50	1.0
1	1	0.75	0.98	1.00
	2	0.80	1.06	1.00
2	1	0.69	0.92	0.96
	2	0.84	1.04	1.00
3	1	0.75	0.88	0.90
	2	0.92	1.01	0.92
4	1	0.91	0.92	0.86
	2	1.04	0.88	0.77
5	1	0.84	0.98	0.96
	2	0.92	1.05	1.06
6	1	0.80	0.99	0.98
	2	0.96	1.08	1.02
7	1	0.76	0.99	1.03
	2	0.88	1.10	1.12
8	1	0.87	0.98	0.89
	2	1.03	1.03	0.95
9	1	0.64	0.87	0.98
	2	0.74	1.02	1.02

Table A5. Replica Means for Change in Whiteness Index (ΔWI) at Each Xenon Exposure Level

FWA	Conc. (% owf)	Rep	Change in Whiteness Index, ΔWI				
			Exposure (AFU's)				
			10	20	40	80	160
Control	0.0	1	-0.2	0.6	1.0	0.4	0.5
		2	0.8	0.8	0.2	0.2	0.1
1	0.05	1	-11.0	-14.6	-20.0	-24.5	-24.9
		2	-10.7	-15.9	-20.6	-23.2	-29.0
	0.50	1	-16.0	-21.4	-28.5	-37.2	-38.4
		2	-15.6	-24.2	-30.2	-43.6	-48.4
	1.0	1	-16.6	-22.0	-29.6	-39.5	-39.5
		2	-15.4	-23.6	-28.4	-34.7	-44.8
2	0.05	1	-10.6	-13.8	-17.9	-21.8	-22.4
		2	-10.8	-15.4	-19.8	-22.4	-26.8
	0.50	1	-13.4	-19.3	-29.2	-34.4	-35.0
		2	-15.8	-22.7	-29.7	-45.2	-47.8
	1.0	1	-16.0	-20.6	-29.2	-38.2	-38.3
		2	-15.0	-22.6	-29.6	-34.9	-44.0
3	0.05	1	-11.8	-16.1	-20.0	-24.7	-26.0
		2	-11.2	-16.6	-21.8	-26.2	-31.1
	0.50	1	-15.9	-22.7	-31.0	-39.8	-40.5
		2	-14.7	-22.8	-30.2	-48.2	-47.2
	1.0	1	-16.8	-23.4	-30.0	-39.6	-41.8
		2	-17.0	-25.8	-32.7	-37.6	-44.4
4	0.05	1	-14.4	-20.6	-26.6	-34.2	-36.6
		2	-14.0	-21.6	-29.0	-35.1	-41.8
	0.50	1	-17.2	-24.6	-35.1	-46.0	-49.4
		2	-16.8	-26.2	-35.2	-53.0	-55.0
	1.0	1	-15.6	-23.4	-32.4	-43.6	-50.0
		2	-16.9	-24.2	-31.8	-38.5	-49.2
5	0.05	1	-13.3	-17.0	-22.2	-27.9	-28.8
		2	-12.6	-18.0	-23.1	-28.2	-32.7
	0.50	1	-19.0	-29.4	-38.4	-49.8	-49.6
		2	-21.9	-31.3	-38.5	-60.2	-57.4
	1.0	1	-19.8	-28.0	-41.4	-54.2	-52.6
		2	-22.4	-33.8	-41.8	-48.8	-56.2

Table A5 cont.

			Change in Whiteness Index, ΔWI				
FWA	Conc. (% owf)	Rep	Exposure (AFU's)				
			10	20	40	80	160
6	0.05	1	-13.4	-17.9	-23.3	-28.4	-29.7
		2	-13.0	-18.8	-24.0	-29.2	-33.6
	0.50	1	-15.4	-21.8	-31.0	-40.0	-39.6
		2	-15.6	-24.8	-31.8	-50.9	-48.6
	1.0	1	-15.8	-22.6	-31.6	-40.3	-42.2
		2	-15.6	-23.6	-31.0	-37.5	-45.3
7	0.05	1	-13.6	-17.0	-21.6	-25.2	-26.0
		2	-14.6	-20.2	-23.8	-26.6	-30.0
	0.50	1	-17.2	-23.8	-31.8	-40.8	-39.2
		2	-18.0	-25.3	-31.6	-44.4	-47.0
	1.0	1	-18.2	-24.7	-32.4	-39.5	-41.8
		2	-18.4	-26.4	-32.6	-38.2	-45.8
8	0.05	1	-13.2	-18.0	-23.7	-29.4	-30.9
		2	-12.8	-19.0	-24.2	-28.2	-35.4
	0.50	1	-18.8	-25.2	-36.8	-49.2	-49.4
		2	-19.9	-31.4	-38.0	-52.5	-58.6
	1.0	1	-19.2	-25.8	-36.6	-49.6	-49.6
		2	-22.0	-33.8	-41.0	-44.5	-51.3
9	0.05	1	-12.0	-14.9	-17.4	-19.2	-19.2
		2	-12.6	-16.1	-18.4	-19.8	-22.2
	0.50	1	-18.0	-23.6	-30.6	-35.6	-35.2
		2	-18.2	-24.9	-30.4	-38.6	-39.4
	1.0	1	-18.4	-24.7	-33.0	-38.8	-38.8
		2	-19.3	-27.5	-33.0	-37.2	-43.7

Table A6. Replica Means for Percentage Change in Whiteness At Each Xenon Exposure Level

FWA	Conc. (% owf)	Rep	Change in Whiteness, %				
			Exposure (AFU's)				
			10	20	40	80	160
1	0.05	1	-40.6	-53.8	-73.2	-89.8	-91.4
		2	-37.7	-56.2	-72.6	-81.8	-102.0
	0.50	1	-37.0	-49.2	-65.6	-85.8	-88.3
		2	-35.3	-54.8	-68.6	-98.9	-109.6
	1.0	1	-37.0	-49.0	-66.2	-88.2	-88.3
		2	-35.1	-54.0	-65.1	-79.4	-102.4
2	0.05	1	-44.8	-57.8	-75.2	-91.4	-94.4
		2	-41.2	-58.6	-74.9	-85.3	-101.7
	0.50	1	-33.6	-48.6	-73.3	-86.4	-87.9
		2	-36.4	-52.4	-68.6	-104.6	-110.4
	1.0	1	-37.8	-48.3	-68.4	-89.8	-90.0
		2	-35.1	-53.0	-69.6	-82.0	-104.2
3	0.05	1	-39.2	-53.6	-66.5	-82.1	-86.6
		2	-34.2	-50.4	-66.4	-79.7	-94.6
	0.50	1	-38.6	-55.1	-75.0	-96.6	-98.2
		2	-36.0	-56.0	-73.8	-118.1	-115.6
	1.0	1	-42.2	-58.9	-75.5	-99.4	-105.2
		2	-43.2	-65.6	-83.1	-95.6	-113.0
4	0.05	1	-34.6	-49.6	-64.1	-82.4	-88.1
		2	-31.7	-49.0	-65.6	-79.6	-94.8
	0.50	1	-42.9	-61.4	-87.6	-115.0	-123.4
		2	-48.2	-75.4	-101.3	-152.4	-158.1
	1.0	1	-44.0	-65.8	-91.4	-122.8	-140.8
		2	-58.7	-84.0	-110.6	-133.8	-170.8
5	0.05	1	-41.6	-53.3	-69.4	-87.2	-90.2
		2	-37.4	-53.0	-68.1	-83.2	-96.4
	0.50	1	-42.7	-66.3	-86.3	-111.9	-111.6
		2	-50.3	-71.9	-88.4	-138.2	-131.8
	1.0	1	-46.8	-66.0	-97.8	-128.0	-124.4
		2	-56.6	-85.4	-105.5	-123.2	-141.8

Table A6 cont.

FWA	Conc. (% owf)	Rep	Change in Whiteness, %				
			Exposure (AFU's)				
			10	20	40	80	160
6	0.05	1	-43.0	-57.3	-74.5	-90.8	-95.1
		2	-39.2	-56.5	-72.0	-87.6	-101.2
	0.50	1	-36.4	-51.4	-73.2	-94.5	-93.3
		2	-34.9	-55.6	-71.5	-114.3	-109.2
	1.0	1	-36.4	-52.1	-72.8	-93.1	-97.5
		2	-36.2	-54.6	-71.6	-86.6	-104.6
7	0.05	1	-52.6	-65.4	-83.2	-97.1	-100.2
		2	-51.3	-71.0	-84.1	-94.0	-105.8
	0.50	1	-41.3	-57.3	-76.6	-97.8	-94.3
		2	-42.3	-59.6	-74.4	-104.6	-110.4
	1.0	1	-41.6	-56.4	-74.1	-90.2	-95.6
		2	-41.9	-60.1	-74.1	-86.8	-103.9
8	0.05	1	-37.9	-51.4	-67.8	-84.0	-88.3
		2	-35.0	-51.8	-66.0	-76.7	-96.4
	0.50	1	-44.0	-59.0	-86.2	-115.0	-115.6
		2	-49.9	-78.8	-95.2	-131.6	-146.8
	1.0	1	-52.6	-70.5	-100.1	-135.8	-135.8
		2	-66.5	-101.9	-123.4	-134.0	-154.4
9	0.05	1	-65.2	-80.9	-94.5	-104.0	-103.9
		2	-61.2	-78.4	-89.6	-96.5	-108.3
	0.50	1	-51.8	-67.7	-87.8	-102.2	-101.0
		2	-50.4	-69.0	-84.2	-107.2	-109.4
	1.0	1	-48.2	-64.4	-86.0	-101.4	-101.4
		2	-48.3	-68.8	-82.6	-93.2	-109.4

Table A7. Replica Means for Change in Relative Fluorescence Intensity (ΔF) at Each Xenon Exposure Level

FWA	Conc. (% owf)	Rep	Change in Relative Fluorescence Intensity, ΔF				
			Exposure (AFU's)				
			10	20	40	80	160
Control	0.0	1	0.00	0.00	0.00	0.00	0.00
		2	0.00	0.00	0.00	0.00	0.00
1	0.05	1	−0.20	−0.25	−0.32	−0.46	−0.52
		2	−0.17	−0.21	−0.35	−0.44	−0.58
	0.50	1	−0.25	−0.34	−0.43	−0.56	−0.58
		2	−0.28	−0.38	−0.50	−0.63	−0.79
	1.0	1	−0.30	−0.38	−0.44	−0.57	−0.60
		2	−0.24	−0.32	−0.43	−0.48	−0.63
2	0.05	1	−0.18	−0.25	−0.33	−0.44	−0.49
		2	−0.24	−0.30	−0.42	−0.53	−0.66
	0.50	1	−0.20	−0.33	−0.44	−0.52	−0.55
		2	−0.19	−0.34	−0.46	−0.63	−0.81
	1.0	1	−0.25	−0.34	−0.43	−0.56	−0.57
		2	−0.27	−0.34	−0.44	−0.50	−0.65
3	0.05	1	−0.18	−0.26	−0.32	−0.40	−0.45
		2	−0.14	−0.28	−0.42	−0.50	−0.60
	0.50	1	−0.22	−0.33	−0.38	−0.50	−0.51
		2	−0.28	−0.38	−0.48	−0.68	−0.70
	1.0	1	−0.26	−0.38	−0.42	−0.50	−0.53
		2	−0.24	−0.32	−0.40	−0.48	−0.56
4	0.05	1	−0.21	−0.34	−0.37	−0.48	−0.54
		2	−0.23	−0.37	−0.48	−0.55	−0.66
	0.50	1	−0.24	−0.37	−0.42	−0.52	−0.56
		2	−0.20	−0.32	−0.40	−0.54	−0.58
	1.0	1	−0.24	−0.33	−0.37	−0.48	−0.52
		2	−0.16	−0.24	−0.30	−0.35	−0.42
5	0.05	1	−0.22	−0.28	−0.38	−0.50	−0.54
		2	−0.23	−0.31	−0.42	−0.52	−0.63
	0.50	1	−0.31	−0.44	−0.46	−0.60	−0.60
		2	−0.33	−0.44	−0.54	−0.73	−0.74
	1.0	1	−0.28	−0.37	−0.46	−0.56	−0.56
		2	−0.37	−0.47	−0.56	−0.62	−0.69

Table A7 cont.

FWA	Conc. (% owf)	Rep	Change in Relative Fluorescence Intensity, ΔF				
			Exposure (AFU s)				
			10	20	40	80	160
6	0.05	1	-0.21	-0.28	-0.40	-0.47	-0.54
		2	-0.27	-0.37	-0.46	-0.58	-0.72
	0.50	1	-0.27	-0.38	-0.50	-0.63	-0.61
		2	-0.24	-0.43	-0.50	-0.81	-0.78
	1.0	1	-0.26	-0.38	-0.46	-0.58	-0.62
		2	-0.27	-0.36	-0.47	-0.54	-0.66
7	0.05	1	-0.24	-0.29	-0.42	-0.54	-0.62
		2	-0.30	-0.39	-0.52	-0.82	-0.76
	0.50	1	-0.34	-0.43	-0.51	-0.69	-0.66
		2	-0.38	-0.49	-0.58	-0.80	-0.94
	1.0	1	-0.35	-0.43	-0.53	-0.64	-0.70
		2	-0.36	-0.48	-0.60	-0.69	-0.84
8	0.05	1	-0.24	-0.31	-0.37	-0.48	-0.54
		2	-0.28	-0.40	-0.50	-0.58	-0.73
	0.50	1	-0.25	-0.38	-0.46	-0.60	-0.59
		2	-0.32	-0.46	-0.49	-0.63	-0.74
	1.0	1	-0.16	-0.32	-0.38	-0.50	-0.50
		2	-0.30	-0.41	-0.48	-0.52	-0.58
9	0.05	1	-0.26	-0.36	-0.47	-0.56	-0.58
		2	-0.28	-0.38	-0.50	-0.59	-0.68
	0.50	1	-0.28	-0.41	-0.52	-0.67	-0.68
		2	-0.36	-0.47	-0.59	-0.85	-0.98
	1.0	1	-0.34	-0.48	-0.60	-0.72	-0.73
		2	-0.36	-0.46	-0.56	-0.65	-0.85

Table A8. Replica Means for Percentage Change in Relative Fluorescence Intensity At Each Xenon Exposure Level

FWA	Conc. (% owf)	Rep	Change in Relative Fluorescence Intensity, %				
			Exposure (AFU's)				
			10	20	40	80	160
1	0.05	1	-26.4	-33.4	-43.4	-61.6	-69.0
		2	-21.6	-26.2	-44.2	-55.3	-72.6
	0.50	1	-25.5	-34.4	-44.2	-57.2	-59.2
		2	-26.7	-36.4	-47.4	-59.8	-74.9
	1.0	1	-29.3	-37.8	-43.8	-57.0	-59.8
		2	-23.8	-31.4	-43.2	-48.8	-62.9
2	0.05	1	-26.8	-36.2	-48.0	-63.2	-71.2
		2	-28.6	-36.0	-50.2	-63.8	-79.2
	0.50	1	-21.6	-36.2	-48.6	-56.6	-60.0
		2	-18.8	-33.5	-45.0	-61.0	-78.2
	1.0	1	-26.0	-35.2	-45.0	-58.0	-59.4
		2	-27.1	-34.4	-43.7	-49.6	-65.2
3	0.05	1	-23.3	-34.5	-41.8	-52.5	-60.2
		2	-14.8	-30.4	-45.4	-55.0	-66.4
	0.50	1	-25.7	-37.9	-44.2	-57.2	-58.2
		2	-27.2	-37.2	-47.7	-68.0	-69.0
	1.0	1	-28.9	-41.5	-46.2	-55.2	-58.8
		2	-26.6	-34.6	-43.5	-52.0	-61.0
4	0.05	1	-23.0	-37.2	-40.8	-52.8	-59.0
		2	-22.3	-35.4	-46.2	-52.4	-63.2
	0.50	1	-26.6	-40.1	-46.1	-57.3	-60.6
		2	-23.0	-36.0	-45.0	-61.3	-66.4
	1.0	1	-28.2	-38.7	-43.2	-56.0	-59.9
		2	-21.0	-31.5	-39.3	-45.7	-55.4
5	0.05	1	-25.6	-34.4	-45.6	-60.4	-64.6
		2	-24.9	-34.0	-46.0	-57.1	-68.2
	0.50	1	-31.3	-44.3	-47.4	-61.4	-61.6
		2	-31.2	-41.8	-51.4	-69.5	-70.0
	1.0	1	-29.0	-39.0	-48.0	-59.3	-58.6
		2	-35.2	-44.6	-52.7	-58.4	-65.6

Table A8 cont.

FWA	Conc. (% owf)	Rep	Change in Relative Fluorescence Intensity, %				
			Exposure (AFU's)				
			10	20	40	80	160
6	0.05	1	-26.6	-35.0	-49.8	-59.3	-68.3
		2	-28.6	-39.0	-47.9	-61.6	-75.0
	0.50	1	-27.2	-39.0	-50.6	-63.6	-61.4
		2	-22.0	-39.8	-46.0	-75.1	-72.6
	1.0	1	-26.4	-38.8	-47.4	-58.6	-62.8
		2	-26.4	-35.6	-45.6	-53.0	-64.8
7	0.05	1	-31.8	-38.2	-55.0	-72.4	-81.6
		2	-34.6	-44.2	-60.0	-71.2	-86.1
	0.50	1	-34.5	-43.4	-51.8	-69.7	-67.4
		2	-34.0	-44.4	-52.0	-72.6	-85.6
	1.0	1	-34.0	-41.7	-51.6	-62.2	-68.6
		2	-32.1	-43.5	-53.6	-61.6	-74.6
8	0.05	1	-27.4	-35.5	-42.5	-54.9	-61.6
		2	-26.8	-38.4	-48.3	-56.7	-71.0
	0.50	1	-25.3	-39.2	-47.2	-61.2	-60.0
		2	-30.6	-44.9	-47.8	-61.3	-72.2
	1.0	1	-18.4	-35.6	-42.7	-56.4	-56.2
		2	-32.1	-43.4	-50.6	-54.8	-61.4
9	0.05	1	-41.0	-55.8	-72.6	-86.8	-90.9
		2	-38.8	-51.8	-67.8	-80.1	-92.5
	0.50	1	-31.6	-47.0	-60.6	-77.0	-78.6
		2	-35.9	-46.4	-58.1	-84.0	-96.6
	1.0	1	-34.1	-49.0	-60.6	-73.5	-74.2
		2	-35.6	-44.9	-55.4	-64.2	-83.6

Table A9. Replica Means for Breaking Strength Values Prior to and Following Xenon Exposure (160 AFU's)

FWA	Concentration (% owf)	Rep	Breaking Strength, lbs Exposure (AFU's) 0	Breaking Strength, lbs Exposure (AFU's) 160
Control	0.0	1	57.0	48.5
		2	55.9	46.3
1	0.05	1	56.6	47.4
		2	53.2	45.0
	1.0	1	53.0	49.0
		2	55.6	47.3
2	0.05	1	52.4	48.0
		2	54.4	47.0
	1.0	1	52.4	48.0
		2	54.2	47.0
3	0.05	1	55.3	48.4
		2	51.2	47.6
	1.0	1	55.9	50.6
		2	55.6	48.6
4	0.05	1	57.6	51.3
		2	53.8	50.0
	1.0	1	57.1	49.0
		2	52.4	48.4
5	0.05	1	54.6	47.8
		2	57.8	48.2
	1.0	1	55.0	49.0
		2	51.5	48.0
6	0.05	1	55.4	48.8
		2	55.4	47.2
	1.0	1	56.2	46.6
		2	53.2	47.2
7	0.05	1	53.8	44.6
		2	55.2	44.1
	1.0	1	54.3	48.2
		2	55.2	47.8

Table A9 cont.

FWA	Concentration (% owf)	Rep	Breaking Strength, lbs	
			Exposure (AFU's)	
			0	160
8	0.05	1	56.6	47.8
		2	54.8	48.4
	1.0	1	54.6	51.4
		2	56.5	50.0
9	0.05	1	56.3	45.8
		2	55.6	44.4
	1.0	1	54.4	47.4
		2	54.4	46.6

Table A10. Replica Means for Percentage Change in Breaking Strength of FWA Treated Samples Before Xenon Exposure Based on Unexposed Untreated Controls

FWA	Rep	Change in Breaking Strength, %	
		Concentration (% owf)	
		0.05	1.0
1	1	-0.6	-6.9
	2	-4.9	-0.5
2	1	-8.1	-7.8
	2	-2.7	-3.0
3	1	-2.9	-1.8
	2	-8.4	-0.4
4	1	+1.2	+0.2
	2	-3.8	-6.2
5	1	-4.0	-3.5
	2	+3.4	-7.8
6	1	-2.8	-1.4
	2	-1.0	-5.0
7	1	-5.5	-4.6
	2	-1.3	-1.2
8	1	-0.5	-4.1
	2	-2.1	+1.0
9	1	-1.2	-4.6
	2	-0.5	-2.6

Table A11. Replica Means for Percentage Change in Breaking Strength of FWA Treated Samples After Xenon Exposure Based on Exposed Untreated Controls

FWA	Rep	Change in Breaking Strength, %	
		Concentration (% owf)	
		0.05	1.0
1	1	-2.4	+1.1
	2	-2.6	+2.1
2	1	-1.0	-1.0
	2	+1.4	+1.6
3	1	-0.2	+4.2
	2	+2.8	+4.8
4	1	+5.7	+1.0
	2	+7.9	+4.4
5	1	-1.6	+1.0
	2	+3.9	+3.6
6	1	+0.6	-3.8
	2	+1.9	+1.8
7	1	-8.0	-0.6
	2	-4.7	+3.2
8	1	-1.3	+5.9
	2	+4.5	+8.0
9	1	-5.6	-2.3
	2	-4.2	+0.6

THE LIGHTFASTNESS OF AND SUBSTRATE PHOTOTENDERING INDUCED BY TRIAZINYLAMINO STILBENE FLUORESCENT WHITENING AGENTS ON COTTON

by

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ABSTRACT

Fluorescent whitening agents (FWA's) improve the whiteness and brightness of textiles by absorbing high energy ultraviolet (UV) radiation and converting it to visible blue light. However, there is greater potential for fading and fiber degradation when the absorption of UV radiation by substrates is increased. This study investigated the relationship between the lightfastness properties and chemical structure of triazinylamino stilbene FWA's and their potential for causing fiber degradation in cotton.

Nine FWA's were applied to cotton at concentrations of 0.05, 0.50, and 1.0% owf, exposed to 0, 10, 20, 40, 80, and 160 AFU's of xenon light and evaluated for changes in whiteness, relative fluorescence intensity, and chromaticity. Samples treated at 0.05 and 1.0% owf and exposed to 0 and 160 AFU's of xenon light were evaluated for changes in breaking strength.

The initial application of the FWA increased the whiteness and relative fluorescence intensity as well as the blueness and redness of the cotton fabric. At the highest theoretical concentration levels (0.50 and 1.0% owf) the fluorescence was self-extinguished for some of the FWA's, decreasing the initial whiteness and fluorescence intensity values. Therefore, data analysis focused on the 0.05% owf concentration level. The actual concentration exhausting out of each theoretical dyebath was different for each FWA due to differences in their chemical structures.

After Xenon exposure the FWA's which had higher actual concentrations present and higher initial whiteness and fluorescence

intensity values generally had better lightfastness. The presence of sulfonic acid groups decreased exhaustion of the FWA´s, initial whiteness and fluorescence intensity values, and possibly lightfastness. As the number of sulfonic acid groups decreased, exhaustion, the initial values, and lightfastness increased. For those FWA´s with a monosulfonated functional group, the location of the sulfonic acid group in the para position on the benzene ring decreased whiteness and fluorescence intensity more than one in a meta position. Hydroxyl groups increased the initial values and the lightfastness of the FWA´s. FWA´s which contained an alkoxy functional group, especially a methoxy group, had significantly better lightfastness than other FWA´s which had higher actual concentrations.

Overall, lightfastness and fiber degradation were not related. However, this could be due to the confounding factors at the higher FWA concentrations because at the 0.05% owf concentration level only, lightfastness was closely associated with changes in breaking strength. As the actual concentration of FWA on the fabric increased at each theoretical concentration level, fiber degradation decreased. Whether this was due to the FWA protecting the fiber or due to differences in chemical structure is difficult to determine since the yarns in the fabrics which contained the highest FWA concentrations appeared to be "glued" together. This would also appear as less of a loss in the strength. Sulfonic acid groups on the FWA molecule tended to increase fiber degradation. FWA´s containing an alkoxy group, especially a methoxy group, had better strength retention even though the actual concentration present was less than that for other FWA´s.