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FLUORESCENT WHITENING AGENTS

The operation of whitening, ie, bleaching or brightening, is concerned with the preparation of fabrics whose commercial value is dependent on the highest possible whiteness. In bleaching, textile converters and paper manufacturers are concerned with the removal of colored impurities or their conversion into colorless substances. In chemical bleaching, impurities are oxidized or reduced to colorless products. Physical bleaching involves the introduction of a complementary color whereby the undesired color is made invisible to the eye in an optical manner, eg, in blueing the yellow cast of substrates such as textiles, paper, sugar, etc, is eliminated by means of blue or blue-violet dyes. Through color compensation the treated product appears whiter to the eye; however, it is actually grayer than the untreated material.

With the aid of fluorescent whitening agents (FWAs), also referred to as optical brighteners or fluorescent brightening agents, optical compensation of the yellow cast may be obtained. The yellow cast is produced by the absorption of short-wavelength light (violet-to-blue). With FWAs this lost light is in part replaced; thus a complete white is attained without loss of light. This additional light is produced by the whitener by means of fluorescence. Fluorescent whitening agents absorb the invisible uv portion of the daylight spectrum and convert this energy into the longer-wavelength visible portion of the spectrum, ie, into blue to blue-violet light (Fig. 1). Fluorescent whitening, therefore, is based on the addition of light, whereas the blueing method achieves its white effect through the removal of light.

A fluorescent whitener should be optically colorless on the substrate, and should not absorb in the visible part of the spectrum. In the application of FWAs it is possible to replace the light lost through absorption, thereby attaining a neutral, complete white. Further, through the use of excess whitener, still more uv radiation can be converted into visible light, so that the whitest white is made more sparkling. Since the fluorescent light of a fluorescent whitener is itself colored, ie, blue-to-violet, the use of excess whitener always gives either a blue-to-violet or a bluish green cast.

The principle of fluorescent whitening was described in 1929 (1), but the industrial use of FWAs began about 10 years later. Since that time FWAs have found increasing use in the most diverse fields (2–5). The toxicological properties of fluorescent whiteners have been summarized (6). Commercial products investigated thus far have been found to be completely harmless. More than 2000 patents for FWAs exist, there are several hundred commercial products, and approximately one hundred producers and distributors.

In 1992, world consumption of FWAs was estimated at 60,000 metric tons. Fifty percent was consumed by the detergent industry, 33% by the paper industry, and 17% by the textile industry. Whitener levels in detergents have stabilized and growth rates track population growth. The paper industry has shown higher growth rates due to a trend to higher whites. The rate of growth has been 4% a year (ca 1992). The textile industry has shown moderate growth (2-4%) largely due to greater usage of cotton fabric. The usage of FWAs in plastics is less than 1% of the total consumption.

Many chemical compounds have been described in the literature as fluorescent, and since the 1950s intensive research has yielded many fluorescent compounds that provide a suitable whitening effect; however, only a small number of these compounds have found practical uses. Collectively these materials are aromatic or heterocyclic compounds; many of them contain condensed ring systems. An important feature of these

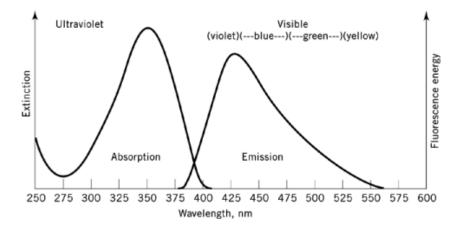


Fig. 1. Absorption and emission spectra in solution of a compound of structure (1).

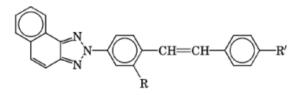
compounds is the presence of an uninterrupted chain of conjugated double bonds, the number of which is dependent on substituents as well as the planarity of the fluorescent part of the molecule. Almost all of these compounds are derivatives of stilbene [588-59-0] or 4,4'-diaminostilbene; biphenyl; 5-membered heterocycles such as triazoles, oxazoles, imidazoles, etc; or 6-membered heterocycles, eg, coumarins, naphthalimide, *s*-triazine, etc.

1. Types of Whitening Agents

1.1. Stilbene Derivatives

Most commercial brighteners are bistriazinyl derivatives (1) of 4,4'-diaminostilbene-2,2'-disulfonic acid (Table 1). The usual compounds are symmetric; preparation begins with reaction of 2 moles of cyanuric chloride derivatives with 1 mole of 4,4'-diaminostilbene-2,2'-disulfonic acid [81-11-8]. Asymmetric derivatives can be synthesized via 4-amino-4'-nitrostilbene-2,2'-disulfonic acid; however, their preparation is more expensive, and they show little advantage over the symmetrical compounds (see Stilbene dyes). The principal effects of structural variations are changes in solubility, substrate affinity, acid fastness, etc. The bistriazinyl compounds are not stable toward hypochlorite; however, some compounds show some fastness after application to the fiber. Mono(azol-2-yl)stilbenes arose from efforts to find hypochlorite-stable products with neutral fluorescence. The bistriazinyl brighteners are employed principally on cellulosics, such as cotton or paper. Some products also show affinity for nylon at the weakly alkaline pH of most commercial detergents.

2-(Stilben-4-yl)naphthotriazoles (**2**) are prepared by diazotization of 4-amino-stilbene-2-sulfonic acid or 4-amino-2-cyano-4'-chlorostilbene, coupling with an ortho-coupling naphthylamine derivative, and finally, oxidation to the triazole.



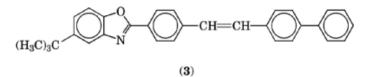
 HO_3S R \mathbf{R}' CH $O_{3}H$ (1) \mathbf{R}' CAS Registry Number Geometricisomer R References 7 [17118-48-8] \mathbf{E} -NHC₆H₅ -OCH₃ [31900-04-6], disodium salt -NHCH₃ (8, 9)---NHC₆H₅ CH_3 [17118-46-6] Е ----NHC₆H₅ (10, 11)CH₂CH₂OH [17118-44-4] Е -N(CH₂CH₂OH)₂ (12 - 14)-NHC₆H₅ [32466-46-9] Е -NHC₆H₅ 15[17863-51-3] Е -NHC₆H₅ 16 -NHC₆H₅ SO₃H NH [16470-24-9], tetrasodium salt -N(CH₂CH₂OH)₂ 17·NΗ [17118-40-0] Е -N(CH₂CH₂OH)₂ (18, 19)SO₃H SO₃H NH [41098-56-0], hexasodium salt SO₃H $-N(CH_2CH_3)_2$ (20, 21)

Table 1. Symmetrical Stilbene Derivatives^a used as Fluorescent Whitening Agents

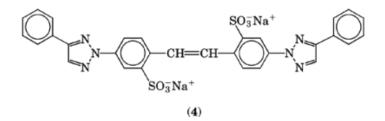
 $^a\mathbf{R}$ and \mathbf{R}' are substituted or unsubstituted amino groups, substituted hydroxyl groups, etc.

With water-solubilizing groups, eg, $-SO_3H$ as in (2a) [4434-38-2] (22), these types of compounds are suitable for whitening cellulosic materials or nylon from soap and detergent baths. In solution and on the substrate these compounds show good fastness to hypochlorite and to light. Water-insoluble derivatives of this family, eg, compounds having the nitrile group as in (2b) [5516-20-1] (23), are suitable for brightening synthetic fibers and resins.

2-(4-Phenylstilben-4-yl)benzoxazoles are prepared by means of the anil synthesis from 2-(4-Phenyl)benzoxazoles and 4-biphenylcarboxaldehyde anil, and used for brightening polyester fibers (24, 25). An example is (3) [16143-18-3].



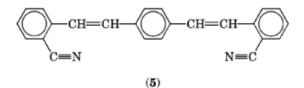
Bis(azol-2-yl)stilbenes (26, 27) such as (4) have been prepared. 4,4'-Dihydrazinostilbene-2,2'-disulfonic acid, obtained from the diamino compound, on treatment with 2 moles of oximinoacetophenone and subsequent ring closure, leads to the formation of (4) [23743-28-4]. Such compounds are used chiefly as washing powder additives for the brightening of cotton fabrics, and exhibit excellent light- and hypochlorite-stability.



1.2. Styryl Derivatives of Benzene and Biphenyl

Other compounds based on the styryl group were prepared to lengthen the conjugated system of stilbene.

1,4-Bis(styryl)benzenes are obtained by the Horner modification of the Wittig reaction, eg, 1,4-bis(chloromethyl)benzene is treated with 2 moles of triethyl phosphite and the resulting phosphonate reacts with 2 moles of *o*-cyanobenzaldehyde to yield (5) [13001-39-3] (28). A strong brightening effect with a reddish cast is obtained on polyester fibers.



4,4'-Bis(styryl)biphenyls are also obtained by the Horner-Wittig reaction of the phosphonate derived from 1,4-bis(chloromethyl)biphenyl and triethyl phosphite with benzaldehyde-o-sulfonic acid, giving the corresponding bisstyrylbiphenyl disodium salt (6) [27344-41-8] (29). They are used in washing powders for brightening cotton to a very high degree of whiteness with improved hypochlorite stability.

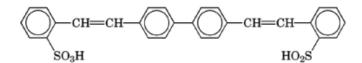
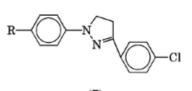


Table 2. Pyrazoline Fluorescent Whiteners^a



CAS Registry Number	R	References
[2697-84-9]	-SO ₃ H	32
[2744-49-2]	$-SO_2NH_2$	(33, 34)
[38848-70-3]	-SO ₂ NHCH ₂ CH ₂ CH ₂ N ⁺ (CH ₃) ₃ -SO ₃ OCH ₃	35
[27441-70-9]	$-SO_2CH_2CH_2SO_3H$, sodium salt $-SO_2CH_2CH_2O$ $-CH$ $-CH_2$ $-N(CH_3)_2$	36
[6608-82-8]	CH ₃	37

^aExamples wherein the chlorinated phenyl ring is substituted have also been made (38, 39).

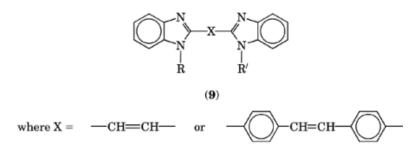
1.3. Pyrazolines

1,3-Diphenyl-2-pyrazolines (7) (Table 2) are obtainable from appropriately substituted phenylhydrazines by the Knorr reaction with either β -chloro- or β -dimethylaminopropiophenones (30, 31). They are employed for brightening synthetic fibers such as polyamides, cellulose acetates, and polyacrylonitriles.

1.4. Bis(benzoxazol-2-yl) Derivatives

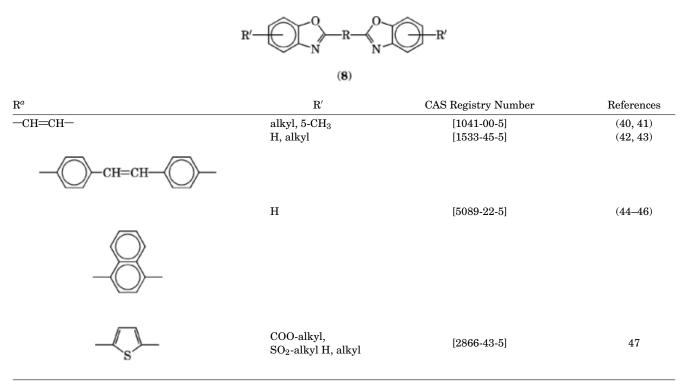
Bis(benzoxazol-2-yl) derivatives (8) (Table 3) are prepared in most cases by treatment of dicarboxylic acid derivatives of the central nucleus, eg, stilbene-4,4'-dicarboxylic acid, naphthalene-1,4-dicarboxylic acid, thiophene-2,5-dicarboxylic acid, etc, with 2 moles of an appropriately substituted *o*-aminophenol, followed by a ring-closure reaction. These compounds are suitable for the brightening of plastics and synthetic fibers.

A large number of patents cover bis(benzimidazol-2-yl) derivatives (9) (48–50). Besides being effective on cotton, compounds of this type show good affinity for nylon.



2-(Benzofuran-2-yl)benzimidazoles may be synthesized by reaction of substituted benzofuran-2-carboxylic acid chlorides with substituted *o*-phenylenediamines and ring closure of the resulting *o*-aminoamide, followed by quaternization (51–54). Such products are brighteners for synthetic fibers, in particular those of polyacrylonitrile.

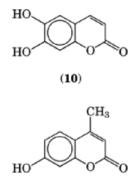
Table 3. Bis(benzoxazol-2-yl) Derivatives



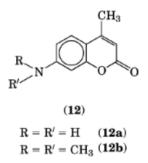
 $^a{\rm R}$ represents the conjugated system of the central nucleus.

1.5. Coumarins.

By treatment of flax with esculin, a glucoside of esculetin [305-01-1] (10), a brightening effect is achieved; however, this effect is not fast to washing and light. The use of β -methylumbelliferone [90-33-5] (11) and similar compounds as brighteners for textiles and soap has been patented.

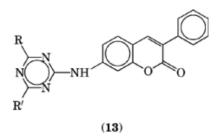






As improvements over β -methylumbelliferone (55–57), 4-methyl-7-amino-coumarin [26093-31-2] (12a) and 7-dimethylamino-4-methylcoumarin [87-01-4] (12b) (58–61) were proposed. These compounds are used for brightening wool and nylon either in soap powders or detergents, or as salts under acid dyeing conditions. They are obtained by the Pechmann synthesis from appropriately substituted phenols and β -ketocarboxylic acid esters or nitriles in the presence of Lewis acid catalysts (see Coumarin).

A further development in the coumarin series is the use of derivatives of 3-phenyl-7-aminocoumarin ((13) where R, R' = Cl or substituted amines) as building blocks for a series of light-stable brighteners for various plastics and synthetic fibers, and, as the quaternized compounds, for brightening polyacrylonitrile (62).

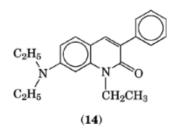


3-Phenyl-7-aminocoumarin is obtained by a Knoevenagel reaction of substituted salicylaldehydes with phenylacetic acid or benzyl cyanide. Further synthesis of the individual end products is carried out by usual procedures.

Other related substances are 3-phenyl-7-(azol-2-yl)coumarins (63–65) and 3,7-bis(azolyl)coumarins (66, 67).

1.6. Carbostyrils

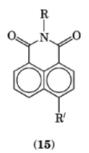
Carbostyrils such as (14) [33934-60-0] are prepared by the reaction of 2-alkylamino-4-nitrotoluene with ethyl glyoxalate in the presence of piperidine, reduction of the resulting 3-phenyl-7-nitrocarbostyril derivatives, and finally methylation of the corresponding amino compounds (68). They are whiteners for polyamides, wool, and cellulose acetates (see Fibers, cellulose esters).



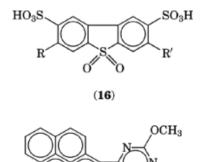
1.7. Other Heterocyclic Systems

Naphthalimides (15), where R' = -NHCOR, are derivatives of 4-aminonaphthalimide (69) and are used in plastics. The alkoxynaphthalimides (15, $R' = OCH_3$) (70, 71) are of particular interest as fluorescent whitening agents.

Naphthalimides are prepared from naphthalic anhydride obtained from naphthalene-1,8-dicarboxylic acid, ie, the oxidation product of acenaphthene or its derivatives, by reaction with amines. They are utilized for synthetic fibers such as polyesters.



A further group of whiteners was found in the acylamino (R,R') derivatives (16) of 3,7diaminodibenzothiophene-2,8-disulfonic acid-5,5-dioxide. The preferred acyl groups are alkoxybenzoyls (72– 74). These compounds give a greenish fluorescence and are relatively weak in comparison with stilbene derivatives on cotton; however, they show good stability to hypochlorite.





OCH₃

Industry	Proportion, $a \%$	Number of fundamentalstructures
textile	20	>30
detergents	45	7^a
paper	35	
synthetic fibers, plastics	1	9^a

Table 4. Use of Fluorescent Whitening Agents

^aValues are approximate.

The pyrene derivative (17) [3271-22-5] is obtainable by the Friedel-Crafts reaction of pyrene with 2,4-dimethoxy-6-chloro-s-triazine, and is used for brightening polyester fibers (75).

Quaternized pyridotriazoles can be used for brightening acrylic fibers (76).

2. Uses

Initially, fluorescent whitening agents (FWAs) were used exclusively in textile finishing; the detergent and paper industries followed thereafter. These products are also used in fiber spinning masses, plastics, and paints.

There are more than a thousand known products derived from 200 compounds based on ca 40 fundamental structures. The approximate use distribution of whiteners is shown in Table 4.

2.1. Textile Applications

A 1971 estimate of world textile fiber consumption (2) showed that approximately 60% of textile goods are dyed and about 30% are whites. The proportion of white goods (>40%) is highest for cotton. These percentages also hold true in the 1990s.

Textile substrates of natural or synthetic fibers are contaminated in the raw state by substances of varying degrees of yellowness. Bleaching is required to remove the yellowish cast. Chemical bleaching agents destroy the yellow coloring matter in fibers. However, even if bleaching processes are carried to the technically acceptable limits of damage to the fibers, they never succeed in completely removing this intrinsic color (see Bleaching agents).

To produce the color white it is necessary to dye with a fluorescent whitener. FWAs used in textiles can be roughly divided into products containing sulfonic acid groups, corresponding to acid dyes, for cotton, wool, and polyamides; cationic whiteners that behave in the same way as basic dyes, for polyacrylonitrile fibers; and whiteners containing no solubilizing groups, corresponding to disperse dyes, for polyester and secondary acetate fibers. This is not a strict division since nonionic FWAs can whiten polyacrylonitrile and polyamide, and certain cationic FWAs produce effects on polyester (77). The second generation of synthetic fibers includes types that have been acid- or base-modified and consequently display different dyeing characteristics (see Dyes, application and evaluation). For dyeing fiber blends such as viscose–polyamide, polyamide–Spandex, or polyester–cotton, only compatible FWAs may be used that do not interfere with one another or have any detrimental effect on fastness properties.

In conjunction with the increased use of synthetic fibers and blends of synthetic and natural fibers, and the modernization of application processes which has taken place simultaneously, the technique of textile whitening has been improved considerably.

Fixing the dye to a fiber can be performed by an exhaust procedure or a padding procedure. In an exhaust procedure the fluorescent whitener is exhausted from a long liquor onto the substrate until an approximate equilibrium is reached between whitener in the bath and whitener on the substrate. In this procedure the

equilibrium is biased primarily toward FWA on the substrate, ie, the highest possible degree of exhaustion is desired. Exhaust procedures are used for loose stock, yarns, woven fabrics, and knit goods which give poor or unsatisfactory results in padding processes, and for garments and garment parts.

Padding methods, ie, application from short liquors, are increasingly important for whitening piece-goods. Woven fabrics or knit goods are passed in an unfolded, open-width state through a small trough charged with treatment liquor containing FWA and subsequently between squeeze rollers to express the liquor to a precisely defined liquor pick-up.

During the drying and, if required, the heat treatment that follows, the fluorescent whitener is fixed on the substrate. FWAs and dyes used in padding procedures must have low substantivity during the padding operation. This is an important prerequisite for level whitening with no tailing.

In contrast to dyes, fluorescent whiteners are not applied exclusively in special processes, but often in combination with bleaching and finishing steps. Fluorescent whiteners used in such processes must be stable and should not interfere with the operation.

The most common chemical bleaching procedures are hypochlorite bleach for cotton; hydrogen peroxide bleach for wool and cotton; sodium chlorite bleach for cotton, polyamide, polyester, and polyacrylonitrile; and reductive bleaching with dithionite for wool and polyamide.

Whitening in combination with the finishing process is used primarily for woven fabrics of cellulosic fibers and their blends with synthetic fibers.

2.2. Detergent Applications

The primary function of FWAs in the laundry process is to whiten fabric load and maintain the original appearance of the white, laundered articles. Laundering is characterized by repeated application to the same item. Fluorescent whiteners used in this repetitive process have to compensate for the reduction in whiteness and contribute toward prolongation of the useful life of the textile material.

In textile whitening there is an unlimited degree of freedom in application, and the processing method can be adapted to suit the optimum color behavior of the substrate. In laundering, the condition of the application bath is predetermined by the composition of the detergent, and the soil loading of the laundry varies from batch to batch. The pH of the washbath is always neutral to alkaline. The bath temperature does not correspond to an optimum dyeing temperature; laundering temperatures vary from cold to boiling water (2). Detergent fluorescent whiteners must remain stable under conditions that prevail during the washing, rinsing, drying, and ironing cycle (2), and they should possess lightfastness. Detergent whiteners must not cause a shade change in the original, generally neutral white of the goods. Fluorescent whiteners that tend to accumulate in excessive amounts on the substrate, thus lending it a greenish cast, are not suitable for use in detergents.

Where laundry is done at boiling point, sodium perborate is added to the detergent as a bleaching agent; in the United States, South Africa, and Australia, sodium hypochlorite is generally added to the washbath; and where laundry is done cold the goods are treated in rinsebaths containing hypochlorite. Only FWAs stable or fast to hypochlorite can be used successfully in these countries (2). The types of FWAs used in the detergent industry are listed in Table 5.

A secondary benefit of FWAs is obtained in improving the appearance of the detergent powder itself. Many significant detergent ingredients are off-white to light yellow in color, resulting in a dull white detergent granule base powder. Through the proper selection and incorporation of a fluorescent whitening agent, the powder aspect can be improved to provide a brilliant white appearance. The bis(styryl)diphenyls (**6**) are especially effective product whiteners.

2.3. Paper Industry Applications

Derivatives of bistriazinylstilbene (1) are used in the paper industry.

$FWAs used^{a}$
(12)
(1) (2) (4) (6) (9)
(7) (8) (12)
(1) (2) (4) (7) (8) (9) (12)
(8)

 Table 5. Fluorescent Whitening Agents in the

 Detergent Industry

^aStructure numbers.

^bGood effects can be obtained only in special processes with high washing and/or drying temperatures.

Substrate	FWAs $used^a$	
polyamide	(1) (3) (5)	
polyester	(2) (8)	
secondary acetate	(8)	
polyacrylonitrile	(2) (7) (9)	
PAN gel whitening	(7) (12)	
poly(vinyl chloride)	(2) (8) (9)	
polystyrene	(2) (8) (9)	
acrylonitrile-butadiene-styrene	(8) (9)	

Table 6. Fluorescent Whitening Agents Used in the Synthetic Fibers and Plastics Industries

^{*a*}Structure numbers.

Most papers are whitened by addition of FWA to both the pulp and surface coating. Roughly one-third of the FWA is added at the pulp stage and the remaining two-thirds are added to the preformed sheet to give surface whiteness. In the first operation, the FWA in aqueous solution is added to the stock at the Hollander or other beater. For this application the products must be inexpensive and readily soluble in water. Besides satisfactory exhaustion at low temperatures, good paper FWAs also require good acid and alum stability as well as compatibility with fillers (qv). Good affinity for pulp is also required, since any unabsorbed FWA is lost in the effluent (see Paper; Papermaking additives; Pulp).

The surface of various types of paper are treated with size coatings and pigment coatings to improve their writability and printability. In some cases, the coating itself may have a low degree of whiteness; in others, a higher degree of whiteness can be obtained with high white pigments. FWAs can be incorporated into size press coatings or off-machine coating operations to enhance the appearance of the finished sheet.

2.4. Synthetic Fiber and Plastics Industries

In the synthetic fibers and plastics industries, the substrate itself serves as the solvent, and the whitener is not applied from solutions as in textiles. Table 6 lists the types of FWAs used in the synthetic fibers and plastic industries. In the case of synthetic fibers, such as polyamide and polyester produced by the melt-spinning process, FWAs can be added at the start or during the course of polymerization or polycondensation. However, FWAs can also be powdered onto the polymer chips prior to spinning. The above types of application place severe thermal and chemical demands on FWAs. They must not interfere with the polymerization reaction and must remain stable under spinning conditions.

In the case of solvent spinning, ie, secondary acetate, polyacrylonitrile, and poly(vinyl chloride), the FWA is added to the polymer solution. An exception is gel-whitening of polyacrylonitrile, where the wet tow is treated after spinning in a washbath containing FWA.

In the case of poly(vinyl chloride) plastics, the FWA is mixed dry with the PVC powder before processing or dissolved in the plasticizing agent (see Vinyl polymers). Polystyrene, acrylonitrile–butadiene–styrene (ABS), and polyolefin granulates are powdered with FWA prior to extrusion (2, 78) (see Styrene plastics; Acrylonitrile polymers; Olefin polymers).

2.5. Measurement of Whiteness

The Ciba-Geigy Plastic White Scale is effective in the visual assessment of white effects (79), but the availability of this scale is limited. Most evaluations are carried out (ca 1993) by instrumental measurements, utilizing the CIE chromaticity coordinates or the Hunter Uniform Color System (see Color). Spectrophotometers and colorimeters designed to measure fluorescent samples must have reversed optics, ie, the sample is illuminated by a polychromatic source and the reflected light passes through the analyzer to the detector.

In order to facilitate rating the preference for white substrates, numerous whiteness equations have been developed based on comparisons of instrumental readings vs visual evaluations. Among the most commonly used equations are those developed by Ganz, ie, W = Y - 800x - 1700y + 813.7, which corresponds to the Ciba-Geigy White Scale (79, 80); Hunter, ie, W = L - 3b; and Stensby, ie, W = L + 3a - 3b (81). In the paper industry, the TAPPI Brightness value often is used as a measure of pulp or paper whiteness. However, the methodology for measuring TAPPI Brightness was developed on nonfluorescent substrates, ie, bleached pulp, and does not fully assess the effects of fluorescent whitening agents. In instrumental comparisons of fluorescently whitened samples, full colorimetric measurements are recommended.

3. Safety and Environmental Aspects

Several studies on FWAs have concluded that diaminostilbenedisulfonic acid/cyanuric chloride (DAS/CC) and distyrylbiphenyl (DSBP) type whiteners are of a low order of toxicity. Their safety has been extensively reviewed by governmental agencies; there is no evidence of human health hazards. FWA producers and users consider these products to be both safe and beneficial to the ultimate consumer. This view is supported by appropriate trade associations. A comprehensive review of available safety and environmental data has been published (82). In addition, principal suppliers are conducting life cycle analyses on the primary whiteners in use (ca 1993).

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HAROLD J. MCELHONE JR. CIBA-GEIGY Corporation

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