Fluorescent Whitening Agents for Modern Detergents

William R. Findley
CIBA-GEIGY Corporation, Greensboro, NC

INTRODUCTION

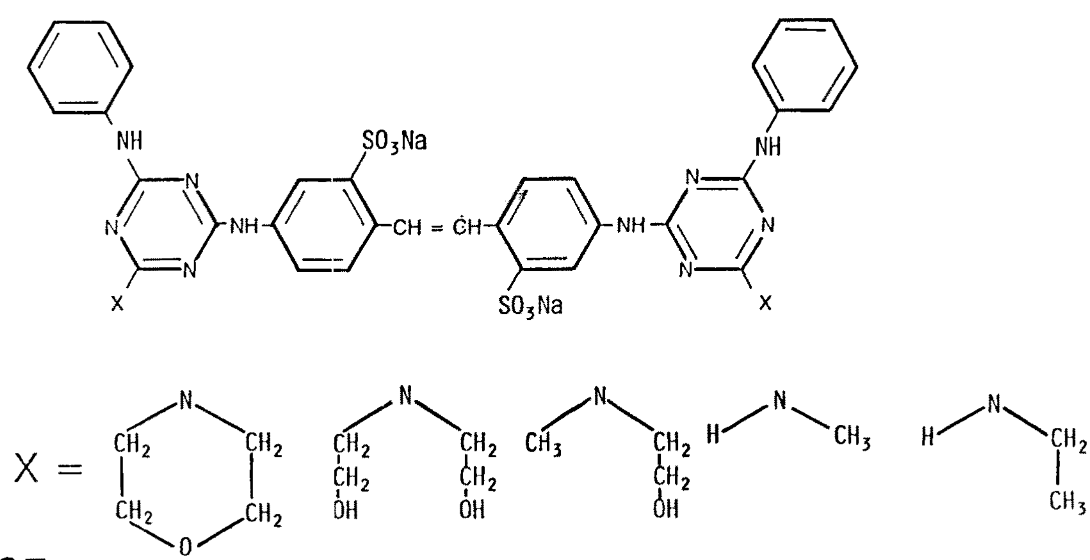
Following the introduction of fluorescent whitening agents (FWA) to the detergent industry, the development and introduction of new products proceeded rapidly. Research chemists synthesized hundreds of new fluorescent compounds in an effort to market improved and/or lower-cost whiteners. The driving force behind these research efforts was the high degree of competition in a new and rapidly expanding market. Fluorescent whitener usage continued to expand in the U.S. until the early 1970s when a number of factors resulted in significant reductions in whitener levels and the removal of synthetic fabric whiteners from many detergents. As total whitener volume declined, the next decade witnessed a reduction in the number of whitener suppliers through mergers and withdrawals from the market. This trend continued through the mid-1980s (1).

During this period, research in the whitener field also declined dramatically. The remaining manufacturers focused on addressing toxicological and environmental issues that were raised in the early 1970s, while product ranges were reduced to those compounds maintaining viable usage volumes in the marketplace. Concurrently, there was little innovation in the detergent industry itself as detergent manufacturers were preoccupied with rising raw material costs and finding suitable phosphate builder substitutes. Few new detergents or significant new formulations were introduced during this period.

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

CURRENT WHITENERS

A comprehensive compilation of all the major whitener structures used in detergents worldwide recently was published by U. Schuessler of Bayer (2). For purposes of this paper, we will review only those that are primarily involved in the new product introductions and applications. Figure 1 shows the major disulfonated diaminostilbene/cyanuric chloride derivatives (DASC whiteners), which continue to hold a dominant position in the U.S. whitener market. Figure 2 shows a tetrasulfonated DASC whitener that is a specialty whitener for detergents, and Figure 3 illustrates the bleach-stable whiteners. Although none of



REFERENCE CODE =	A	B	C	D	E
ASTM CODE =	DASC-3	DASC-2	DASC-4	—	—

FIG. 1. Disulfonated diaminostilbene/cyanuric chloride whiteners.

REFERENCE CODE | ASTM CODE
F | —

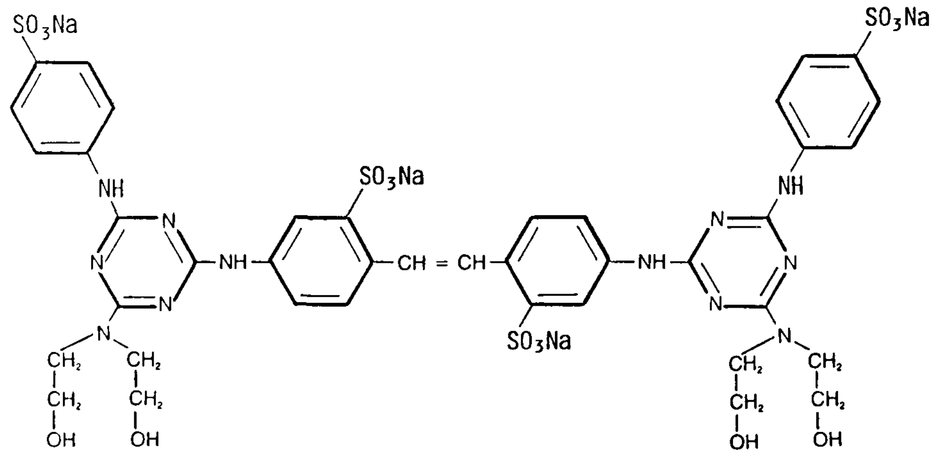


FIG. 2. Tetrasulfonated diaminostilbene/cyanuric chloride whitener.

REFERENCE CODE	ASTM CODE
G	DSBP-1
H	—
I	—
J	NTS-1

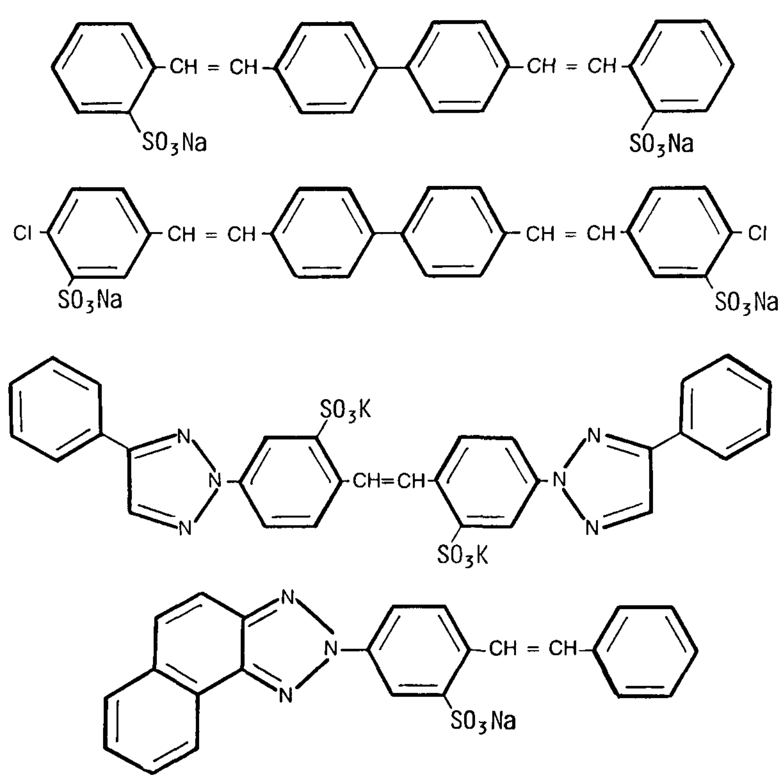


FIG. 3. Bleach-stable whiteners.

these compounds is new, modifications are being explored continuously to optimize incorporation and performance in modern detergent formulations.

PHYSICAL FORMS

A recent evolutionary development has taken place in the U.S. market, which in reality has been catching up to the European manufacturers. In the 1970s, all major European FWA producers installed new or modified existing spray-drying products as opposed to the previous fine powders. This change in physical form was readily accepted by the detergent industry because it alleviated handling problems and significantly reduced dusting in the workplace environment. In the U.S., however, the whitener drying equipment installed was not readily adaptable to produce bead-form products, and the total replacement of the existing spray towers was considered prohibitively expensive. Alternative technologies were investigated, and in 1985 Ciba-Geigy introduced free-flowing, low-dusting granular forms of compounds A (DASC-3) and C (DASC-4) produced by an agglomeration process with fluid bed drying. This same type of process is receiving increasing attention in the detergent industry as a potential alternative to spray-drying detergent powders (3). During 1988, compound B (DASC-2), already available in bead-form, will become available in an agglomerated version. Also, compound J (NTS-1) now is available in both powder and granulated forms.

With very few exceptions, the bead or granular whiteners have become the standard physical form on a worldwide basis. In addition to the obvious advantage of reduced exposure to airborne dusts, the flowability of these products permits the use of automated solids metering devices that are becoming more prevalent in modernized detergent plants. Such devices often cannot handle the traditional powder forms. The areas where the free-flowing forms cannot be used generally involve blending or mixing operations with shear insufficient to pulverize or disperse the agglomerates. The increasing popularity of liquid detergents, of course, has raised the issue of supplying whiteners in liquid form. Structure F in Figure 2, in fact, is supplied normally as an approximately 17%-active aqueous solution. In the case of most disulfonated DASC and bleach-stable whiteners, however, total solubilities are limited and it is impossible to make a stable solution with a high, practical, active ingredient concentration without the use of unacceptable solvents, hydrotropes or surfactants. The economics of transporting and storing relatively dilute solutions is also an important factor. An alternative to a true solution is the preparation of high active dispersions; this approach is being used in the U.K. No dispersions stable enough for transport over long distances or extended storage have been developed for the U.S. market.

Research into improved liquid versions is continuing. Currently, however, it is most economical to convert powders to stock solutions or dispersions in the detergent manufacturing plant and subsequently meter these into the final formulation.

LIQUID DETERGENTS

The most dynamic and dramatic change occurring in the detergent industry is the explosive growth of liquid detergents. Even in Europe, where the liquid segment was considered stagnant or declining as late as mid-1986, renewed product introductions and promotions have propelled liquids into a strong growth position. The primary factors affecting whitener selection for liquids are solubility and the usage of nonionic surfactants. Acceptable FWA must be sufficiently stable upon storage. For example, compound A (DASC-3), a major whitener for powder detergents, is difficult, if not impossible, to incorporate in most liquids. The formulator must focus on the more soluble compounds such as structures B, D, E, G and I, but also must maintain sufficient substantivity for optimum performance. The nonionic surfactants used in liquid detergents can solubilize a whitener to such an extent as to adversely affect the fiber to wash liquor equilibrium, thereby reducing whitener effectiveness. The final selection will be dependent upon the overall ratios of anionic surfactant, nonionic surfactant, and electrolytes or builders in the formulation. The effects of cationic surfactants, which are included in a number of liquid detergents, will be discussed in the next section.

A new factor in the selection of FWA for liquid detergents—a factor that is essentially irrelevant for powders—has been the subject of at least two patents (4,5). Many liquid detergent labels recommend the use of the product as-is as a pre-spotter or stain remover before general laundering of the item. The application of a highly concentrated whitener solution to a limited area on a garment or linen can leave a fluorescent spot or stain. This stain is especially apparent on pastel or earth-tone textiles and does not level or disappear during the wash cycle. The patents indicate that the structure J, as well as structures K and L as shown Figure 4, were among the first whiteners ever used and led the way to universal whitener usage in detergents. They may now become two of the most "modern" products as well.

COMBINATION PRODUCTS

Currently, a major challenge to the whitener research chemist is the development of FWA that are compatible and efficient in the presence of cationic surfactants and antistatic agents. Since the introduction of cationic fabric softeners, the detergent manufacturers have had to make-do with the standard whiteners in spite of the inherent incompatibility of the anionic FWA and cationic surfactant, as well as the quenching of fluorescence by the cationic surfactant. Generally, the most soluble anionic whiteners are used with cationics to assure compatibility. With rinse-additive fabric softeners, a relatively low FWA performance can be tolerated because the primary fabric whitening is accomplished in the wash cycle. In the case of combination detergent/softeners, however, the whitener system must deliver total and acceptable performance in spite of the presence of the cationic surfactant.

Of the combination products available today, those formulated to include anionic surfactants and builders or other electrolytes can use a traditional whitener such as compound B (DASC-2), which previously was used only in rinse-additive fabric softeners. Although the efficiency of the FWA is somewhat reduced, adequate whitening performance can be achieved at viable whitener concentrations.

A far more difficult problem is presented by the nonionic/cationic low-electrolyte liquid detergents in which adequate whitening performance is impossible to achieve with current FWA. The highly soluble tetrasulfonated

REFERENCE CODE — ASTM CODE

K — —

L — DASC-1

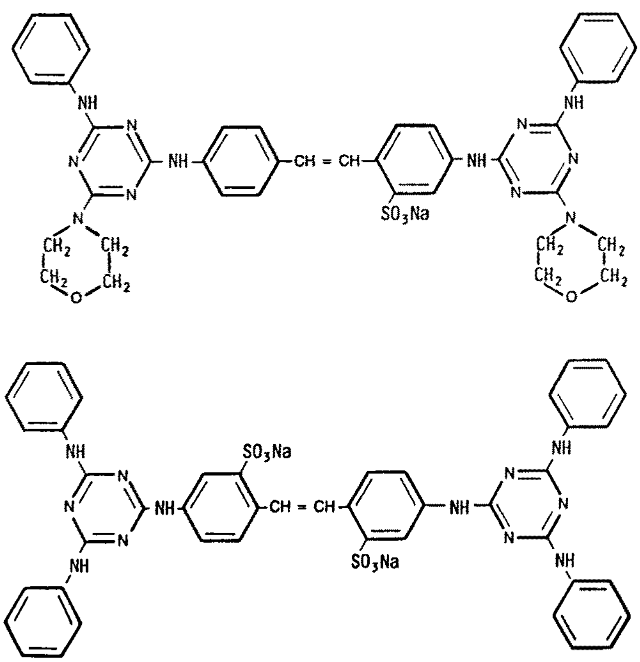


FIG. 4. Reduced "staining" whiteners.

REFERENCE CODE — ASTM CODE

M — —

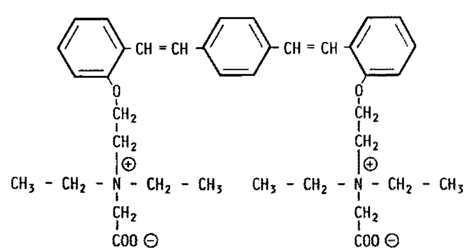


FIG. 5. Distyrylbenzene amphoteric whitener.

DASC type (structure F) is compatible with such formulations, but performance efficiency is very low. It would appear logical to assume that the solution to the problem would be the synthesis of cationic whiteners for both compatibility and functionality. Unfortunately, the introduction of a cationic functional group into a whitener structure most often results in a significant reduction in fluorescence similar to the quenching effect of cationic surfactants. However, recently a distyrylphenyl-based amphoteric compound that is shown in Figure 5 that maintains excellent performance characteristics in nonionic/cationic formulations has been deveoloped (6). This development compound currently is undergoing extensive evaluations in the detergent industry on a worldwide basis. Also, research chemists are continuing to explore alternative compounds for this growing application.

CONVENIENCE PRODUCTS

Almost as a corollary to the expanding liquid and combination product market has been the introduction of several convenience products packaged or presented in premeasured single-dose units. These products range from nonaqueous detergent slurries in water-soluble polymer packs and detergent-impregnated nonwoven sheets to multifunctional nonwoven packets of detergent, bleach and softener. It is too early to predict the ultimate total impact of these convenience forms on the market; the traditional FWA have proven effective in all products to date. Additional developments in these areas, however, will be monitored closely for new whitener opportunities.

BLEACHES

The remaining area of change in the detergent industry that has presented another major challenge to the whitener research chemist is the growing use of aggressive oxygen bleaches. For many years, the terms "bleach unstable" and "bleach stable" as applied to whiteners referred only to their susceptibility to destruction by dilute hypochlorite in solution. All whiteners were considered stable to oxygen bleach, which was essentially defined as sodium perborate. However, the introduction of activated perborates, percarbonates, peracids and hydrogen peroxide bleaches has completely changed this definition. No longer can the DASC-type whiteners be considered to be stable in oxygen bleaches; only the compounds represented by structures G, H, I and J can be recommended. Even these compounds may be slowly destroyed by certain formulations, and new compounds will be needed. Unfortunately, no new compounds are available at this time, but research efforts are continuing.

FUTURE POSSIBILITIES

Following a relatively long period of consolidation and product range rationalization, the fluorescent whitener manufacturers have increased efforts to develop new whiteners for the detergent industry. Unlike the original development of today's fluorescent whiteners, which was driven by the chemists' interest in synthesizing new basic structures and a highly competitive expanding marketplace, the current impetus is based primarily on new product and formulation innovation by the detergent industry. These new formulations are establishing technical requirements for FWA that cannot be fulfilled by existing products. Major new development challenges have been identified in the areas of liquid detergents, combination products and bleaches. Additional challenges are sure to be identified in the future.

It should be noted, however, that the introduction of new products will be tempered by the realities of today's regulatory climate. Fluorescent whitening agents are, by definition, specialty chemicals with a relatively predictable and limited volume market potential. The enormous costs of the toxicological and environmental studies required to market a new product will preclude product introduction on speculation. More than ever, the successful development of new whiteners will depend on close partnerships between the suppliers and the detergent manufacturers to assure that technical and performance requirements are met and costs are under control. Although we expect to continue to rely heavily on the current FWA in the market, it is encouraging to see new innovations in the detergent industry and a resumption of new whitener research to complement these developments.

REFERENCES

1. Findley, W.R., *J. Am. Oil Chem. Soc. 60*:1367 (1983).
2. Schuessler, U., *Proceedings of the Second World Conference on Detergents*, edited by A.R. Baldwin, American Oil Chemists' Society, Champaign, IL, 1986, p. 187.
3. Dolan, M.J., *HAPPI 24 (7)*:64 (1987).
4. U.S. Patent No. 4,559,169.
5. European Patent Application 0273119.
6. U.S. Patent No. 4,478,598.

This paper was presented at The Soap and Detergent Association's 1988 annual convention.