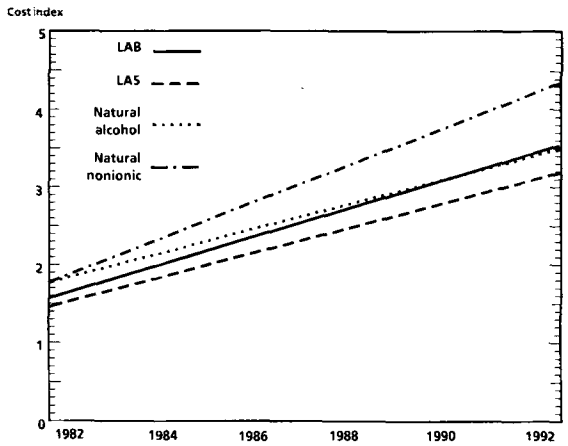

FIG. 8. Comparative analysis of US manufacturing costs of surfactant chemicals.

Most Relevant to Formulators

Carrying the base-case economic model a step further, the outlook for the surfactant products derived from LAB (like LAS) and natural alcohol (like nonionic ethoxylate) were projected.

Figure 8 shows comparative manufacturing costs of LAB and natural alcohol with LAS (linear alkylbenezene sulfonate) and natural alcohol nonionic ethoxylate, the actual ingredients used by detergent formulators.

Comparison is on a 100% active basis. Natural nonionic ethoxylates' cost trend is above that of natural alcohol because it is made by exchanging relatively expensive ethylene oxide for relatively inexpensive natural alcohol. On the other hand, to produce linear alkylbenezene sulfonate, LAB is reacted with sulfuric acid or SO_3, which is relatively inexpensive. As a result, the overall cost of LAS (100% active basis) actually drops because the added molecule is less costly than even LAB and is considerably less costly than ethylene oxide.

Whitener Selection for Today's Detergents

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ABSTRACT

The ultimate choice of a whitener or whitener system for a specific formulation often represents a compromise between the optimum technical performance desired and economic considerations. This overview provides an introduction to fluorescent whitening agents to those new to the field of laundry product formulations and, perhaps, serves as a refresher course for the more experienced formulator. In actual practice, the selection of an optimum whitener system is based on extensive laboratory trials and evaluations.

INTRODUCTION

Fluorescent whitening agents (FWA), formerly designated "optical brighteners," were introduced into the detergent industry during the early 1950s. By the end of the decade, their penetration of the detergent market was universal, but at generally low usage levels. The 1960s witnessed an explosive growth in whitener consumption as suppliers introduced improved products and detergent manufacturers vied for greater market shares with "whiter than white" advertising campaigns. During this period, the detergent manufacturers could select whiteners from among ca. 20 discrete chemical structures offered by six major suppliers. In the 1970s, however, the whitener level trend reversed, resulting in a gradual decrease in consumption. The primary factors involved in this trend were: changing promotional strategies; raw material economics; changing wash load composition; builders (nonphosphate) reformulation; and toxicological/ecological factors.

As a result, the number of suppliers and chemical entities offered have been essentially cut in half. In spite of the reduced consumption, however, fluorescent whitening agents, like the "active" surfactants, remain as a universal ingredient in heavy duty home laundry detergents.

FACTORS INFLUENCING WHITENER SELECTION

Before discussing whitener selection for specific applications, it is beneficial to review several general factors involved in the selection process. It is the variability in these properties which differentiates one whitener from another.

Total Solubility

In general, effective FWA exhibit relatively low total solubility. Since fabric whitening by exhaust procedures is an equilibrium process, a limited solubility enhances fabric deposition. On the other hand, a low solubility limit of some whiteners may preclude their usage in liquid formulations.

Rate-of-Solution

This factor is operative only in powdered laundry products and is reflected primarily in low-temperature performance characteristics. Although a specific whitener may be totally soluble at wash liquor concentrations, the time required to achieve total solubilization, especially at low temperatures, may well exceed the normal wash cycle limit of 10 min. Therefore, the total potential whitening effect expected for a given FWA concentration may not be achieved.

Detergent Whitening

The primary function of a laundry product whitener is to enhance the appearance of white fabrics. A secondary factor that must be considered, however, is the effect of the FWA on the appearance of the laundry product itself. Product appearance is dependent on whitener selection, the type of formulation, and the method of incorporation.

Bleach Stability

In a classical sense, the chemist may consider the term "bleach stability" as a measure of a compound's inherent resistance to oxidation. In relation to FWA, the term has a much narrower definition, specifically the resistance of a whitener to destruction in solution by hypochlorite. All

whiteners are relatively stable to hypochlorite when bound to the fiber surface, but vary widely in their response to hypochlorite in solution. This factor is important when evaluating the effects of misuse of bleach by the consumer.

Formulation Compatibility

Another major factor in whitener formulation is consideration of FWA compatibility. Variables such as surfactant type, pH, and electrolyte content often will be the primary basis for specific whitener selections.

TODAY'S FLUORESCENT WHITENING AGENTS

Let us review the commercially available products and their properties as they relate to the selection factors listed above. Rather than use trade names, I have chosen to use ASTM code designations as listed in ASTM Publication DS53A, "List of Fluorescent Whitening Agents for the Soap and Detergent Industry."

Bleach Stable Cotton Whiteners

An example of a bleach stable cotton whitener, DSBP-1 is shown in Figure 1. Technically, DSBP-1 represents the "state-of-the-art" in whitener technology. Its advantages include high fluorescence efficiency, bleach stability, high lightfastness, and good solubility. This unique set of properties makes DSBP-1 an almost universal candidate for all home and institutional laundry products, both powders and liquids.

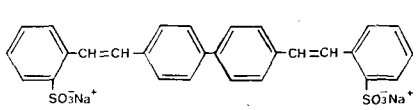
Bleach Unstable Cotton Whiteners

Three examples of bleach unstable cotton whiteners are shown in Figure 2. These diaminostilbene/cyanuric chloride derivatives represent the "workhorse" whiteners of the US detergent industry. The three products are primarily differentiated by their solubility characteristics, both total solubility and rate-of-solution.

DASC-3, the morpholine derivative, exhibits the lowest solubility and generally the slowest rate of solution. Since incorporation in liquid formulations is difficult, and often impossible, the compound is used primarily in powder detergents. It exhibits optimum performance at wash temperatures above 100 F.

DASC-4, the N-methylethanolamine derivative, is a moderately soluble compound with a fast rate-of-solution. Like DASC-3, the product is used primarily in powder detergents although its solubility is adequate for incorporation in some liquid formulations. The fast rate-of-solution imparts excellent low temperature performance making DASC-4 a true "all temperature" whitener.

DASC-2, the diethanolamine derivative, is the most soluble compound of the series. It is generally marketed in the acid, rather than the sodium salt, form and requires neutralization for incorporation. DASC-2 is the traditional choice for rinse additive fabric softeners and is recommended for liquid detergents. It is not widely used in alkaline heavy-duty powders due to a tendency to yellow the product and diminished performance at high wash temperatures.



DSBP-1

FIG. 1. Bleach stable cotton whitener.

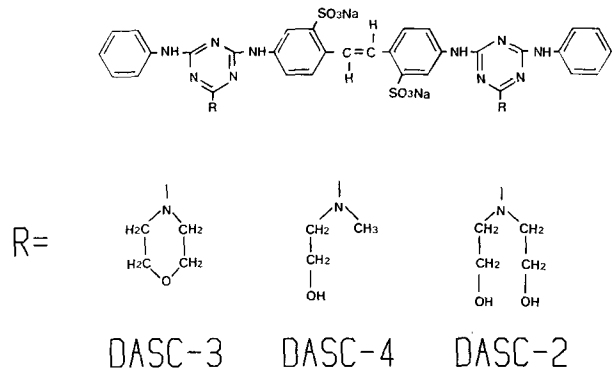


FIG. 2. Bleach unstable cotton whiteners.

Fine Fabric Whiteners

Two examples of fine fabric whiteners are shown in Figure 3 and both are primarily effective on polyamide fibers. NTS-1, a sulfonated naphthotriazoylstilbene, is most often used in combination with one of the above cotton whiteners in powder laundry detergents. Although NTS-1 has been used successfully in liquid formulation, its limited solubility in water presents problems in incorporation. The more highly soluble C-2, a coumarin derivative, is recommended for light-duty liquids specifically intended for the hand-washing of nylon and wool apparel.

While discussing the area of "fine fabric" whitening, some comments on polyester whiteners are in order. Although such products were available and used in the 1960s, their life span in the detergent industry was relatively short due to the following factors:

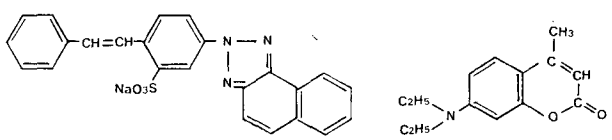
– All polyester fiber manufactured for white goods is mass whitened with compounds which essentially last the life of the fabric.

– Effective exhaust whitening of polyester cannot be achieved below 140 F.

– The nonionic type FWA used for dyeing polyester present potential bioaccumulation problems in fish.

To the best of my knowledge, no polyester whiteners are employed in today's laundry products.

This list of specific structures is not intended to be all-inclusive. Other compounds are offered by individual suppliers, but are not published in the ASTM handbook. In most cases the performance properties of these products fall into one or more of the general categories above.



NTS-1 C-2

FIG. 3. Fine fabric whiteners.

Heavy-Duty, Built, Detergent Powders

Heavy-duty, built, detergent powders continue to dominate the US home laundry detergent market and, as expected, primarily utilize the diaminostilbene-based "workhorse" whiteners, DASC-4 and DASC-3. The solubility, detergent whitening, and fluorescence efficiency characteristics of these FWA are ideally suited to both anionic- and nonionic-based built powder systems with DASC-4 providing excellent "all-temperature" whitening performance. Recommended use levels range from 0.1 to 0.5% on the weight of the detergent. Alternatively, DSBP-1 yields similar performance at lower concentrations (0.05-0.25%), with the added advantages of bleach stability and high lightfastness. Where nylon whitening is desirable, the inclusion of 0.02-0.1% NTS-1 is recommended.

Heavy-Duty Liquid Detergents

The primary factors governing the selection of whiteners for liquid detergents are total solubility, pH and ingredient compatibility. The relatively insoluble whiteners DASC-3 and NTS-1 are not readily incorporated into liquid detergents without the addition of organic cosolvents or hydrotropes. On the other hand, the highly soluble DSBP-1 and DASC-2 whiteners can be dissolved easily in most heavy-duty liquid formulations, while DASC-4, a "workhorse" FWA in powders, is stable and effective in most unbuilt (low-electrolyte) liquids. If nylon whitening is desired, a low concentration (0.05-0.1%) of C-2 can be incorporated.

Light-Duty Detergents

Since light-duty detergents are intended to launder lingerie, hosiery, etc., a straight cotton whitener is normally omitted. The two fine fabric whiteners, C-2 and NTS-1, are recommended for liquid and powder light-duty detergents, respectively. At concentrations of 0.05-0.15%, both compounds provide adequate nylon whitening along with limited performance on cellulosics.

Fabric Softeners

The major factor in the selection of whiteners for cationic fabric softeners is ingredient compatibility. All of the FWA discussed are anionic in nature and tend to interact with cationic surfactants to form high molecular weight, insoluble organic salts. Of the diaminostilbene derivatives, the highly soluble DASC-2 (at levels of 0.1-0.2%) has been the product of choice for fabric softeners, although incorporation procedures must be carefully controlled to attain satisfactory product stability. The newer distyrylbiphenyl derivative, DSBP-1, is even more compatible, and yields equivalent performance at approximately half the concentration of DASC-2.

In addition to the inherent anionic/cationic incompatibility, the fluorescence efficiency of all whiteners is diminished, or "quenched," by cationic surfactants. The rational for incorporating a whitener in a rinse additive softener is not to achieve an additive whitening effect on the laundered goods, but to maintain at least the effects imparted by the detergent in the wash cycle.

Bleaches

All whiteners are stable in sodium perborate and other oxygen bleaches and the recommendations parallel those for heavy-duty powder detergents. DASC-3 and DASC-4 at 0.05-0.15% levels or DSBP-1 at 0.02-0.08% levels are the recommended cotton whiteners. Since dry oxygen bleaches are generally promoted for "fine fabrics," the inclusion of 0.02-0.05% NTS-1 is desirable, especially in view of the reduced usage of nylon whiteners in today's heavy-duty detergents.

In the area of chlorine bleaches, no FWA is stable in commercial strength liquid hypochlorite. Although the "bleach stable" whiteners, DSBP-1 and NTS-1, can be incorporated into dichloro-isocyanurate dry bleaches, shelf life stability is limited, especially in the presence of atmospheric moisture.

Commercial Laundry Products

The various products used in commercial laundry operations frequently contain whiteners. The FWA levels are dependent on the amount of laundry product used on a given weight of fabric, i.e., the lower the product usage, the higher the whitener content. Recommendations are summarized as follows: Soaps/detergents, 0.1-0.5%, DASC-3; 0.1-0.5%, DASC-4; 0.05-0.25%, DSBP-1. Antichlor, 5-10%, DASC-4; 1-5%, DSBP-1. Acid sours, 0.5-2%, DSBP-1. Softeners, 0.1-0.3%, DASC-2; 0.05-0.15%, DSPB-1.

Nonionic/Cationic Detergent/Softeners

Finally, the newest product category in the detergent industry is the liquid detergent/softener combination. Such products represent a challenge to the whitener producer in the factors of FWA compatibility and fluorescence "quenching" by the cationic component.

Whiteners DSBP-1, NTS-1, and DASC-2 have all been incorporated successfully in such formulations, but exhibit sharply reduced "whitening" efficiency. Efforts are under way to develop alternative FWA which will provide whitening performance comparable to regular anionic heavy duty detergents at an acceptable cost level.

THE FUTURE

The whitener industry is a mature industry. Product rationalization has trimmed the available compounds to the workhorse range and eliminated low volume specialty products. In addition, all of the products discussed have undergone extensive, and expensive, toxicological and environmental testing. It is estimated that comparable evaluations of a new whitener would cost between $1 million and $2 million. These factors certainly inhibit the development and introduction of new whiteners, especially on a speculative basis.

Fortunately, the range of whiteners currently available fully satisfy the technical requirements for most of the detergent industry products. The impetus for the development of new FWA will lie in the introduction of new formulations, such as the liquid detergent/softeners, where an optimally effective FWA is not available.