⁂ Minor Additives in Heavy-Duty Laundry Detergents

O.W. NEIDITCH, Lever Brothers Company Research Center,
45 River Road, Edgewater, NJ 07020

ABSTRACT

A number of heavy-duty detergent additives, collectively referred to as "minor additives," are ingredients which are individually present in minor amounts but which can contribute significantly to the performance and marketability of detergent products. In this paper, additives which will be discussed include fluorescent whitening agents (FWA), soil antiredeposition agents and perfumes.

INTRODUCTION

Minor additives are detergent ingredients which are present individually in minor amounts but which can contribute significantly to the performance and marketability of heavy-duty laundry detergents. They are defined as those ingredients used in the formulation of heavy-duty laundry detergents at levels less than 5% and most often at levels less than 1%. A list of minor additives is shown in Table I.

The functions of the minor additives include improving performance, improving stability, facilitating processing and improving the aesthetics of heavy-duty laundry detergents. This paper is limited to a brief discussion of the role of perfumes, fluorescent whitening agents (FWA) and antiredeposition agents in these detergent products.

TABLE I

Minor Additives in Heavy-Duty Laundry Detergents

Bacteriostats
Bleaches
Bluing agents
Borax
Buffers
Colorants
Corrosion inhibitors
Enzymes
Fabric softeners and antistatic agents
Flow promoters
Fluorescent whitening agents
Hydrotropes
Opacifiers
Perfumes or fragrances
Processing aids
Soil antiredeposition agents
Starches
Suds control agents

PERFUMES OR FRAGRANCES

Perfumes—or fragrances, as they are called by those in the perfume industry—serve several functions in a heavy-duty laundry detergent. At a minimum, the perfume should mask the base odor of the detergent ingredients and the package. Beyond this requirement, a perfume can provide an initial good impression when the consumer opens the package. Obviously, an unpleasant base odor or a poor perfume impression when the package is first opened can turn off the consumer before s/he has a chance to evaluate the performance of the product in laundering. Another function of a perfume is to cover the odor of soils and provide a pleasant odor in the laundry area during the wash. A perfume can be selected to provide a pleasant, clean odor to clothes after washing and even after drying. Finally, the perfume can provide a "halo effect" which reinforces perception of performance, particularly with respect to such attributes as, e.g., fresh and clean.

Heavy-duty laundry detergents vary in their requirements for perfumes because of their range in alkalinity, ingredients, form (powders and liquids) and packaging (1). For example, a nonphosphate powder detergent containing sodium carbonate and sodium silicate may have a pH of 11.0 in solution and a built, heavy-duty liquid detergent may have a pH of 11.0 in the container. The alkalinity of these formulations limits the type of ingredients which can be used in perfume formulations for these products. Esters which can be hydrolyzed by alkalies are found in most jasmine, lavender, rose, fruity and some floral fragrances, and thus limit the selection of these types of perfumes.

Perfume ingredients also can affect the foaming characteristics of a formulation. Materials such as α-terpineol and hydroxycitronellal can affect foam quality, as will certain other polar molecules.

Perfume ingredients can, in themselves, have strong colors or react among themselves or with traces of iron to change the color of a detergent product.

Perfumes can be lost from a powdered detergent formulation by escaping through a permeable cardboard box. Liquid detergents packaged in plastic bottles can react with or migrate through the plastic, resulting in loss of perfume, collapse of the container, or deterioration of the perfume and the container.

The level of perfume in detergent products ranges from the 0.1-0.125% necessary for providing base coverage to the 0.2-0.25% in some of the new market introductions. Detergent ingredients can affect the level of perfume required (C.M. Young, personal communication). Because perfume oils tend to be subdued by nonionic surfactants, greater perfumery effort is required to develop suitable perfumes. The U.S. detergent industry uses ca. 9 million lb/year of perfumes for granular detergents and 6 million lb/year for liquid detergents (2).

Two perfume trends are predominant in U.S. detergents: citrus and floral-lavender. The major powdered detergent had a lilac-green perfume but changed to a green-citrus-floral scent which is flagged on the package as a "New Fresh Clean Scent." Detergent perfumes are unlikely to change to extreme types never before incorporated. Floral and citrus, predominantly lemon or verbena, will be popular detergent fragrances for quite some time.

It is desirable to use a perfume which leaves a fresh, clean odor on laundry after washing and drying. Because the laundry may consist of a wide variety of fabrics, including cotton, nylon and polyester, the perfume must be substantive across this range of hydrophilic and lipophilic fabrics. Future perfume considerations may well be based on the retention properties of particular essential oils, and the technology of the perfume manufacturers (1).

FLUORESCENT WHITENING AGENTS (FWA)

A fluorescent whitening agent (FWA) is defined by the American Society for Testing and Materials (ASTM) as a compound which, by its presence in or on a near-white substrate, creates a visual whitening effect by fluorescence (3). FWA also have been called white dyes, optical dyes, optical brighteners, optical bleaches, fluorescent dyes, fluorescent bleaching agents, fluorescent brighteners and brighteners. The term "fluorescent whitening agent" is now generally accepted as the best descriptive name for these compounds (4).

When FWA are present on fabrics, they absorb invisible ultraviolet light which is present in daylight and many artificial light sources and emit longwave, visible bluish violet light. When FWA are applied to white fabrics which have acquired a yellowish cast, the blue-violet light emitted by the FWA provides a whiter appearance by additive mixture. This helps to restore the original whiteness of fabrics without the need for excessive use of bleaches which could damage fabrics.

FWA which are used in heavy-duty laundry detergents belong to several chemical classes, but all have certain features in common. These features include: (a) a conjugated, planar double bond system; (b) monomolecular distribution; (c) substantivity to fabrics; (d) the ability to absorb ultraviolet radiation between 300-400 nm (but not above 410 nm) and to emit visible blue light between 400 and 500 nm with maximal emission around 430-436 nm. In addition, FWA must meet other criteria, e.g., safety, stability, compatibility, solubility and cost (5).

The major class of FWA used in the U.S. in heavy-duty laundry detergents is the diaminostilbenedisulfonate-cyanuric chloride derivatives (DAS/CC) (Fig. 1). Only the relatively stable, planar, *trans*-form of these FWA is substantive to fabrics and exhibits the desired fluorescence. The predominant group of DAS/CC derivatives used is the 4,4′-bis[(4-anilino-6-substituted-1,3,5-triazin-2-yl)amino]stilbene-2,2′-disulfonic acids in which the substituted group is either morpholino (Fig. 2), hydroxyethylmethylamino (Fig. 3), dihydroxyethylamino (Fig. 4), or methylamino (Fig. 5). These derivatives differ, to varying degrees, in water solubility, reduction of effectiveness by nonionic surfactants, coloration of detergent powders and chlorine bleach stability. Some of these properties are influenced as much by the crystalline form of the FWA as they are by the nature of the substituted chemical group. The β-modification of the FWA crystals is manufactured by new technology resulting in a low-color product which is stable to storage (6). These crystals reduce problems of coloration of white detergent powders. Dust-free, free-flowing granules with good water solubility, produced by spray-drying, also have been developed.

The DAS/CC types described are strongly substantive to cellulosic fibers and are very hypochlorite-bleach-stable once they are attached to the fibers. They are, however, very unstable to hypochlorite bleach in solution, so that bleach addition must be delayed for ca. 5 min into the wash cycle to allow sufficient time for the FWA to attach to the cellulosic fibers. Some of the DAS/CC derivatives are also moderately substantive to nylon. The DAS/CC derivatives are extremely unstable to light in dilute solution and moderately unstable to light on fabrics, especially when wet, as during drying. Other types of FWA are available when bleach stability or light stability are important factors in laundering.

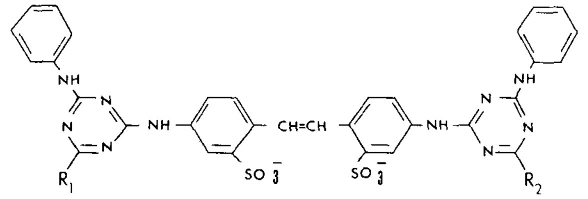

FIG. 1. Diaminostilbenedisulfonate-cyanuric chloride derivatives (DAS/CC). The major class of fluorescent whitening agents (FWA) used in heavy-duty laundry detergents in the U.S. R_1 and R_2 = substituted amine groups.

In 1974, of a total of 12.15 MM lb (100% active basis) of FWA used by the soap and detergents industry, 76% or 11.0 MM lb (100% active basis) were DAS/CC derivatives. The 12.15 MM lb represents 14.82 MM lb of selling-grade material based on an average activity of 82% for the FWA, as used by the soap and detergent industry. The inert ingredients include common salt, Glauber salt, soda ash, water and solvents.

Another major type of FWA is a naphthotriazolylstilbene whitener (NTS) (Fig. 6). The specific example used in heavy-duty laundry detergents is the sodium salt of 5-(2H-naphtho[1,2-d]triazol-2-yl)-2-(2-phenylethenyl)-benzenesulfonic acid. This FWA is substantive to cellulosic and polyamide fibers and is stable to hypochlorite bleach. Use of this FWA in detergents has declined in recent years and is now used mainly in some liquid products.

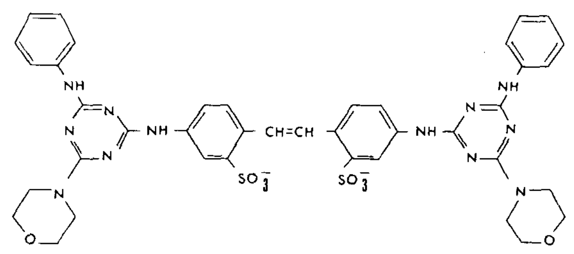

FIG. 2. A DAS/CC derivative in which the substituted groups are morpholino groups.

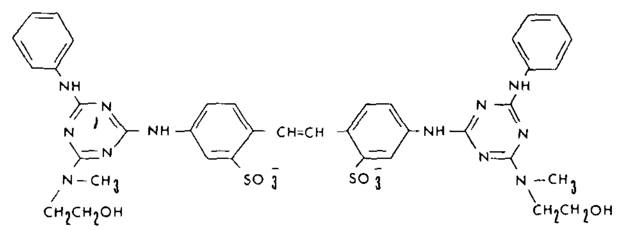

FIG. 3. A DAS/CC derivative in which the substituted groups are hydroxyethylmethylamino groups.

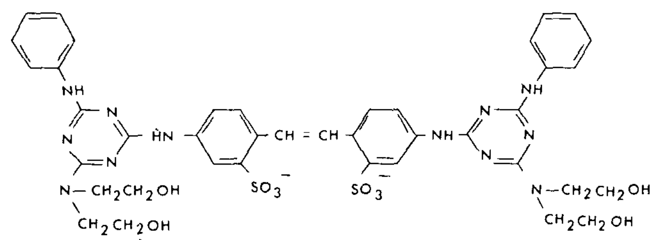

FIG. 4. A DAS/CC derivative in which the substituted groups are dihydroxyethylamino groups.

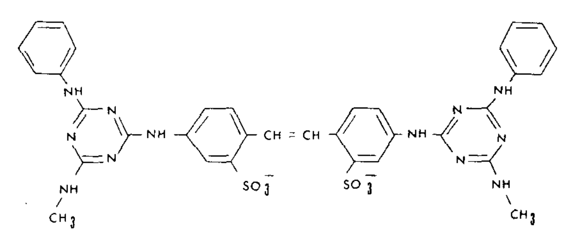

FIG. 5. A DAS/CC derivative in which the substituted groups are methylamino groups.

A newer FWA which is in more limited use is a stilbene triazole FWA (Fig. 7). The specific example used in heavy-duty laundry detergents is 4,4'-bis(4-phenyl-1,2,3-triazol-2-yl)-stilbene-2,2'-disulfonic acid disodium salt. This FWA is substantive to cellulosic and polyamide fibers and is very stable to hypochlorite bleach and to light.

The last major type of FWA used in heavy-duty laundry detergents is a distyrylbiphenyl (DSBP)-type (Fig. 8). The specific example used is 2,2-(4,4'-biphenylene divinylene)-dibenzenesulfonic acid, disodium salt. This FWA is substantive to cellulosic fibers and also is very stable to hypochlorite bleach and light.

Other types of FWA are used in small quantities for brightening of synthetics other than nylon.

Levels of FWA in heavy-duty laundry detergents have been as high as ca. 1% (100% active basis). Beginning in 1976, FWA in many products began to drop to levels below 0.2% in most leading products. The Bureau of the Census' *1977 Census of Manufactures* shows a drop in the delivered cost of FWA from \$27.2 MM in 1972 to \$4.9 MM in 1977 for the soap and detergent industry.

Recently, liquid detergent products have been introduced which are based on a nonionic surfactant plus a cationic softener. The conventional anionic FWA are inactivated by the cationic in such systems. In one case, no FWA was found in the product, whereas a nonionic-type FWA was found in another product. One FWA manufacturer is sampling a cationic FWA which is claimed to be effective in the nonionic/cationic active system. If this FWA proves to be effective and safe to use, another FWA may be added to the list of useful fluorescent whitening agents for heavy-duty laundry detergents.

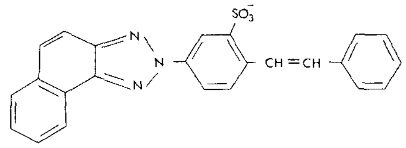

FIG. 6. A naphthotriazolylstilbene (NTS)-type FWA.

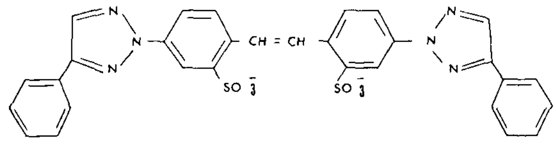

FIG. 7. A stilbene triazole or diphenyltriazolylstilbene (DPTS)-type FWA.

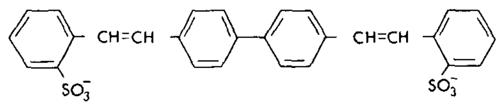

FIG. 8. A distyrylbiphenyl (DSBP)-type FWA.

ANTIREDEPOSITION AGENTS

Soil redeposition is defined by ASTM as deposition of removed soil on a surface during a cleaning process (7). Whiteness retention also is defined by ASTM as comparative whiteness of original and cleaned fabric (8).

Soil suspending or antiredeposition agents are added to synthetic detergent formulations to help the surfactant hold soil particles in suspension and to prevent them from settling back on fabrics (9).

Soil redeposition and its prevention is not strictly a property related to the presence or absence of antiredeposition agents, but is primarily dependent on the type and amount of surfactants and builders present in the formulation. This is true both for particulate and oily soil redeposition. The ability of a solution of a detergent to prevent the precipitation of particulate soil, which has been removed from a fabric, and the redeposition of the particulate soil back onto the same or another fabric has been shown to be related to the combination of surfactants and builders which make up the major part of the formulation. The builders can both cause and help prevent redeposition of soil (10).

Another group of minor additives in detergents are certain additives used for improving the prevention of soil redeposition during laundering.

The synthetic detergent derived from petrochemicals came into wide usage as a replacement for soaps because of a shortage of fats during World War II. While soaps have excellent antiredeposition properties, the synthetic detergents do not, and require an additive to improve these properties. This led to the commercial use of sodium carboxymethylcellulose, commonly abbreviated CMC or SCMC in detergent formulations. SCMS is a polymer prepared commercially by reacting cellulose with alkali and chloracetic acid. Sodium carboxymethyl groups ($-CH_2CO_2Na$) are thereby introduced into cellulose, which is itself a polymer made up of anhydroglucose units.

The solubility of SCMC is a function of the degree of substitution of the OH groups on cellulose by the glycolic acid group. The number of sodium carboxymethyl or glycolic acid groups introduced per anhydroglucose unit can be determined and is known as the degree of substitution (DS). A DS between 0.4 and 0.8 leads to the best antiredeposition performance (11,12). If the DS exceeds 0.8, the SCMC is too water-soluble and not sufficiently adsorbed onto cotton to give effective antiredeposition performance. If the DS is reduced below 0.4, the solubility decreases rapidly, causing a marked reduction in antiredeposition properties (12).

The viscosity of SCMC is a function of the length of the cellulose molecule employed in making the SCMC. The length of the polymer is usually quoted as the degree of polymerization (DP). A DP in the range of 200-500 is desirable.

An important feature of SCMC is that it is a polyelectrolyte and therefore displays an electrostatic charge in an aqueous solution. While there has been considerable controversy as to the mechanism by which SMCM acts as an antiredeposition agent (10), it is now generally believed that SCMC acts by adsorption onto cotton and also onto clay soil. This increases the electrostatic repulsion between the negatively charged cotton and soil particles. The antiredeposition effect becomes less as the size of the soil particles decreases. Once very small-sized particles have deposited on the fabric surface, they are extremely difficult to remove. This partly explains why SCMC is not completely effective in preventing particulate soil redeposition on cotton.

Detergent-grade SCMC usually is not purified and can contain up to 40% salts, mainly sodium chloride and sodium glycolate, and sometimes sodium sulfate.

In addition to SCMC, several other polymers have been tested for use as antiredeposition agents for cotton. These include polyvinyl alcohol (PVA), polyvinylpyrrolidone (PVP), gliadin (a protein), polyvinyloxazolidone, polyoxyethylene glycol (PEG) (10), and copolymers of methylvinyl ether with maleic anhydride (13). Some of these have been used or are currently in use in some detergent products.

Cotton fabrics in the U.S. have been largely replaced by synthetics (mainly polyester) or blends of synthetics with cotton. The blends are almost always treated with one or more polymeric materials to impart a "durable press" finish, soil-release properties and softness. These fabrics differ considerably from cotton in their susceptibility to particulate and oily soil redeposition. SCMC is only slightly effective or completely ineffective in preventing soil redeposition on these newer fabrics. Oily soil redeposition is a particular problem for synthetics and blended fabrics and has been mitigated to some extent by the treatment of these fabrics with various soil-release finishes at the textile mills. Nevertheless, oily soil redeposition on synthetics and blends, and release of oily soils and stains from these fabrics, continues to be major problems in laundering.

Greminger et al. (14) described experiments in which cellulose ethers such as methylcellulose, methyl hydroxypropyl and methyl hydroxybutyl cellulose were tested as antiredeposition and soil-release agents for polyester fabrics. Their data show considerable benefits for the addition of these cellulose ethers to a nonionic/carbonate detergent. In this particular example, the interaction between the surfactant and the hydroxybutyl methylcellulose was stated to be the critical factor in achieving antisoiling on polyester fabric. Their review of the patent literature points to a trend of using nonionic cellulose ethers containing increased levels of hydrophobic substitution to achieve both improved antiredeposition and soil release on synthetic fibers such as polyester.

Greminger (personal communication) noted that significant commercial acceptance of hydroxybutyl methyl cellulose as a detergent additive has resulted in the commercialization of this product.

Current research on methyl cellulose and its modifications involving interfacial tension measurements, using the spinning drop technique which allows observation of equilibria factors, show a correlation between the degree, the distribution, and the hydrophobicity of the substitution on the cellulose background, and the key benefit of inhibition and removal of oily staining on polyester and other synthetic fabrics (G.K. Greminger, Jr., personal communication).

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Detergent Enzymes: Developments during the Last Decade

C.A. STARACE, Industry Sales Manager, Novo Laboratories, Inc., Wilton, CT 06897

ABSTRACT

The decade of the seventies saw dramatic changes in the formulation of heavy duty laundry detergents. The reduction in the STPP content in laundry product formulations was a notable example. During the early 1970s, heavy duty liquid laundry detergents were introduced and today represent an estimated 20% of the heavy duty laundry detergent market. A significant trend during this decade toward lower wash temperatures also appeared. These developments in home laundry products and washing trends have been followed by collateral developments in detergent enzyme technology. During the 1970s, a new generation of high alkaline, active detergent enzymes were developed. This new group of alkaline proteases were characterized by greater activity and stability under conditions of alkalinity between pH 10.5 to near 12, thus favoring phosphate-free detergent formulations. These enzymes also were found to exhibit superior stability in nonbuilt liquid laundry detergent systems. Safety considerations at the plant operation level have resulted in a continual improvement in the quality of coated and encapsulated detergent enzyme granulates. During the past 10 years, detergent enzymes have passed through three generations of physical forms, from the powders to prills to encapsulates. The decade of the 1980s offers exciting possibilities for enzymatic laundry products. The trend toward lower wash temperatures, caused initially by the popularity of synthetic fabrics, is being compounded by a radical reappraisal of household energy consumption patterns. In this new atmosphere of energy conservation, detergent enzymes will offer energy-saving options in an assortment of laundry products. Finally, as we start this decade of the 1980s, the spiralling cost of petrochemical feedstocks will cause us to rethink laundry product formulations and here again, detergent enzymes offer an important alternative for the future.

Laundry detergent products have undergone changes in product formulation over the last 10 years. These changes have been well publicized (1), especially with regard to the shift toward reduced and zero-content sodium tripolyphosphate formulas (2). The trend to lower phosphate laundry products brought with it substitution or replacement builders, including sodium carbonate, sodium silicate, zeolite, NTA and others.

Another important development during the 1970s was the major growth of heavy duty liquid detergents. Liquid laundry detergents have gained substantial acceptance in the American household and, as the decade of the seventies closed, this product group held an estimated 20% market share (3). These liquids consist of two groups: those with builders and those without.

With the exception of the nonbuilt liquid products, heavy duty laundry detergents emerging in the mid-1970s were notably higher in alkalinity. For example, major U.S. detergent products in 1968 containing 49% sodium tripolyphosphate (4) exhibited a wash water pH of ca. 9.2. A