Optical Brighteners as Detergent Additives

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Abstract

Laundering with brightener-free detergents generally restores, but does not improve, the initial whiteness of soiled white fabrics. Optical brighteners are needed to increase the total spectral radiance, which normally results in better whiteness and an impression of superior cleanliness. Today's quality detergents therefore contain optical brighteners, often at levels higher than 0.5%. The outlay for brightener at this level represents a significant portion of the total raw-material cost. Proper evaluation and selection of brightener systems (1–5) is therefore important. Selection is related to detergent type, laundry habits, fiber content of the wash load, the hue of white preferred by housewives, and other factors. These factors tend to change. For example, in recent years, cold-water washing has become more popular in the United States; the capacity of washing machines has increased; bleach dispensers have been added; more polyamide and polyester, resin-treated cotton and blended fabrics have been introduced; and improved surfactant/builder systems have been developed for detergents. New brightener systems have, of necessity, been adopted. Changes will no doubt continue. The detergent industry will consider these changes carefully and will have to update brightener systems to comply with the new conditions.

Why Are Brighteners Used?

FABRICS ARE LAUNDERED for reasons of health, cleanliness, and appearance. The presence of light-absorbing soils is most easily observed on white and pastel-colored substrates because white and off-white surfaces have relatively high light reflection in the visible wavelength region. It has therefore become customary to evaluate the performance of a detergent on white fabrics.

A detergent free of optical brightener can increase the reflectance of soiled substrate only to a level approximately equal to the pre-soiled level. Bleach in the laundry liquor can assist in soil removal and provide a higher-than-initial fabric reflectance.

Fig. 1 shows the relative spectral radiance curves, against $BaSO_4$, of soiled cotton (whiteness, W, equal to 54.6), soiled cotton washed once with a brightener-free detergent (W = 69.9), soiled cotton washed with a brightener-free detergent and hypochlorite bleach (W = 71.9), soiled cotton washed with commercial detergent containing brightener (W = 93.0), and soiled cotton washed with commercial detergent and bleach (W = 89.4). The whiteness values given were obtained from Hunter Colorimeter measurements by using the $W = L + 3a - 3b$ function (discussed later). The use of detergent and bleach results in a fabric with higher reflectance than soiled cotton. The total light energy coming from the fabric is higher still when brightener is used.

Repeated washings of soiled cotton with brightener-free detergent and bleach would eventually result in a fabric reflectance similar to that of unsoiled cotton (W = 99.4). The contributions of brightener to total spectral radiance of unsoiled cotton, after one wash with commercial detergent alone (W = 134.6), and commercial detergent plus bleach (W = 119.6) are shown in Fig. 2.

Theoretically the maximum reflection that can be obtained by removal of light-absorbing bodies is 100% (measured against MgO) at all wavelengths between 400–700 nm. In practice however, even a reflection of 92–95% at all wavelengths in the visible region is hard to reach. Also this type of "neutral white" is not necessarily the white preferred by the average housewife. "Whites" are preferred with a higher radiance in the 420–450 nm region than in other ranges of the visible spectrum; this is the region in which naturally yellowed substrates show a deficiency in reflectance. Optical brighteners that exhibit their strongest emission in this region are able to compensate for the deficiency in blue reflectance of the substrate and to contribute additional radiance to produce the appearance of preferred whites. This is precisely why brighteners are used in detergents.

The sensory impression of "whiteness" of a brightened substrate (2) is caused both by light reflected by the fabric and light emitted by the brightener.

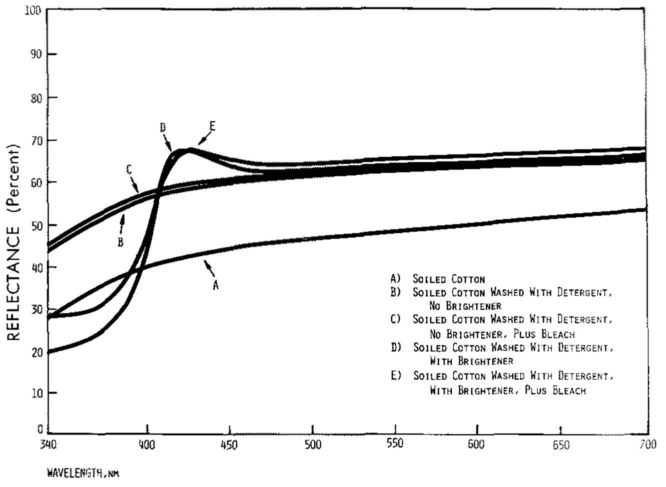

FIG. 1. Radiance of soiled cotton.

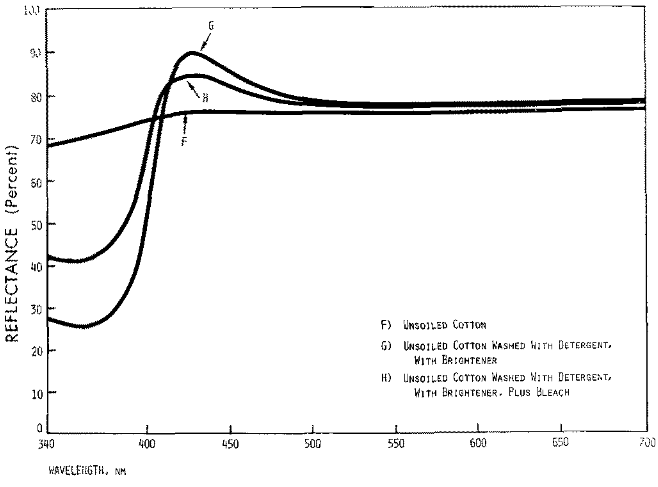

FIG. 2. Radiance of unsoiled cotton.

Many factors contribute to this sensation. The color of the base substrate and the contribution of the brightener vary with light source, surface properties, gloss, transparency, and moisture content of the substrate, the geometry of illumination and observation, and other factors. Consequently the brightener will not always be able to contribute the type of emission required to approximate the preferred hue of white.

Whiteness Preference

The exact form of the radiance curve related to the most preferred white varies from observer to observer because of psychological and physiological differences (2). Unfortunately there is little reliable information on preferences for brightened white fabrics of different hues and lightness levels. It is said that the average U.S. housewife prefers a bluish white with a slight violet cast (6), but there are few published data to substantiate this. The "preferred" white might even vary in color at different geographical locations. Also, women's preferences regarding whiteness (7) may change from time to time.

Goldwasser (8) found that brightened fabrics of reddish or greenish hue were either most or least preferred; bluish fabrics seemed least likely to be on either extreme of the preference scale; and "neutral" fabrics were ranked better than, equal to, and inferior to the other hues.

Vaeck (9) concluded that the preferred whites are those of high luminosity and high blue content (limit unknown) and that some observers prefer reddish-blue hues of white whereas other observers prefer greenish-blue hues.

Whiteness Evaluation

Realistically whiteness, in terms of the preferred appearance of a fabric, can be evaluated only by visual comparison of one white substrate with another. The opinion of a large number of observers (under standardized conditions) is required to arrive at an average valid response. Fortunately comparisons of visual and instrumental findings have enabled investigators to develop instrumental techniques for the evaluation of whiteness that duplicate more or less accurately visual results.

Visual Comparisons

The relative effectiveness of brighteners or brightener systems can best be determined by panel testing. Randomly selected female observers appear to be the best judges (3,10). Fabrics can be evaluated by ranking from "most white" to "least white," by paired comparison, or by any proven statistically based method.

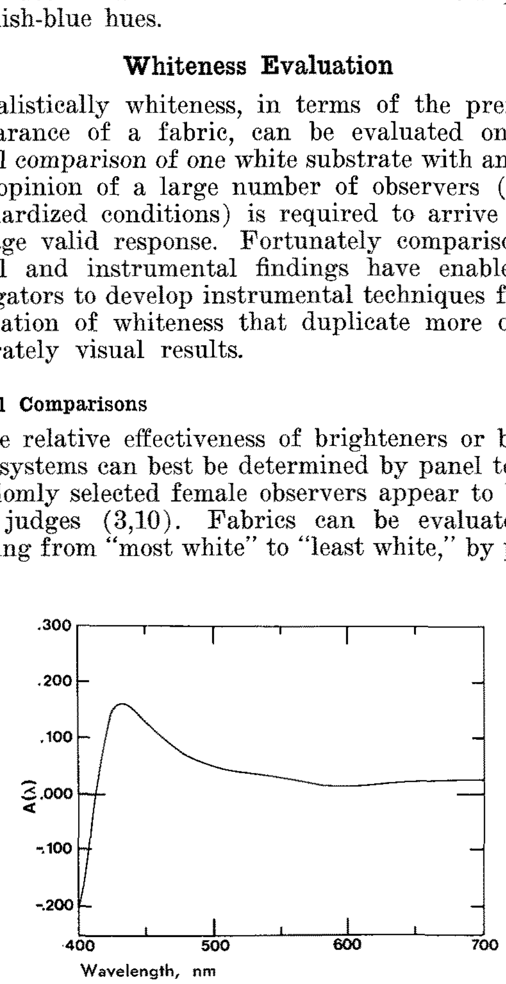

FIG. 3. Spectrum weighting function [from F. Grum and J. M. Patek, TAPPI *48*, 357 (1965)].

TABLE I

Whiteness Functions

Functions	Authors
1. $W = \sum_{400}^{700} P(\lambda)A(\lambda)\Delta\lambda + K$	Grum
2. $W = Y + kE$	Vaeck
3. $W = 2B - A$	Stephansen
4. $W = G/3 + (B - A)$	Berger
5. $W = 4B - 3G$	Taube
6. $W = L - 3b$	Hunter
7. $W = L + 3a - 3b$	Stensby

Some companies determine the whiteness of laundered swatches by visual comparison with a whiteness scale. The whiteness scales (ranging, for example, from 0 to 260) consist of a series of brightened fabrics of increasing whiteness (11). Treated swatches are compared with the scale, under standard lighting conditions, by specialists. The weakness of this method is related to the specialist's preference for a certain hue, which may not necessarily be the preference of the average U.S. housewife.

Instrumental Measurements

Three types of instruments are customarily used to evaluate brightened fabrics: fluorometers, tristimulus colorimeters, and spectroreflectometers. Fluorometers measure gross fluorescence values; these values provide no indication of spectral radiance and, strictly speaking, should be used only to compare the effectiveness of brighteners having the same excitation and emission characteristics, and then only within a concentration range in which the hue remains constant.

The tristimulus colorimeter provides a better approximation of the relative whiteness exhibited by brighteners or brightener systems. However this instrument is not well suited to recording small differences in emission spectra of brighteners; such differences are registered on the observer. Only a continuous recording instrument, such as the Beckman DK-2A spectroreflectometer with reversed optics, can furnish information on the total spectral radiance of brightened fabrics, and then only for an arbitrarily chosen light source.

A large number of whiteness functions for transferring measurements into meaningful whiteness values have been suggested, and some are in use (3). Many however are valid only for a single plane in color space or in the limited area for which they were developed. It must also be kept in mind, when using any of these whiteness functions, that at a certain, as yet undetermined, distance from the achromatic point in the chromaticity diagram, at least in the green, yellow, and red direction, the functions lose their validity. The white converts into a color at this point. The same is true for the vertical luminosity (Y) axis in going from white toward black. At one value of Y (around 70) the sample no longer appears white but grey. Most recently suggested and frequently used whiteness functions are shown in Table I.

Grum (12) proposed a new and interesting approach to a whiteness value, based on measurements. The relative radiance value at selected wavelengths (taken from such curves as those shown in Figs. 1 and 2) is multiplied by a weighting factor, and the sum of the products is calculated. The weighting function shown in Fig. 3 was found to give the most favorable correlation between calculated values and

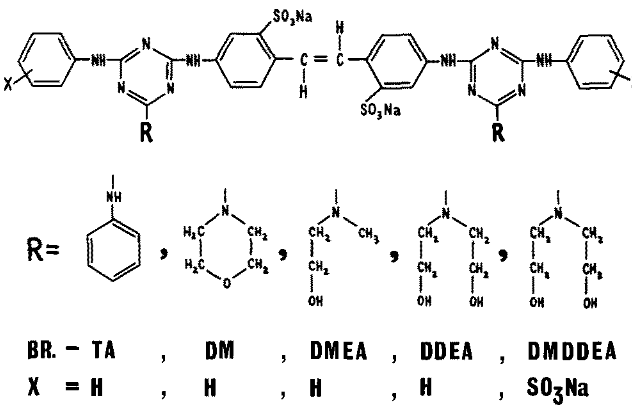

FIG. 4. CC/DAS brighteners.

visual whiteness. The curve indicates that whites with high radiance around 435 nm are preferred.

Vaeck (9) found that a nearly perfect correlation with average visual whiteness can be obtained by a linear combination of the luminosity Y and a value E derived from the chromaticity of the sample (k is a constant):

$$W = Y + kE$$

Correlation between whiteness calculated by the Stephansen and Berger functions and visual whiteness is good only in the case of fabrics with brighteners of similar hue. In the United States brightened fabrics are frequently measured on a Hunterlab Model D40 (two-filter) instrument, and whiteness is calculated by the function suggested by Taube. The $W = L - 3b$ equation (measured by using a Hunterlab Model D25 instrument, for example) introduced by Hunter, is nearly identical to the Taube function.

The function suggested by Stensby (3) indicates that white substrates of high luminosity and reddish-blue hues are preferred. In most cases, the function gives good correlation with visual evaluation of brightened substrates.

Although all the above whiteness functions have limitations, they furnish a good indication of relative whiteness in defined areas. They are time-saving compared with visual evaluation and are satisfactory for preliminary screening. Final results should however be confirmed by visual comparison.

Brightener Chemistry

More than 200 chemically different optical brighteners are commercially available worldwide. The number of chemically different brighteners contained in the patent literature is several times larger than this and growing rapidly. The general chemistry and performance properties of many of these chemical types have been discussed previously (1,13–20). The following will deal therefore only with the more important brightener types which are currently used in laundering products in the United States. These brighteners may be classified as cotton brighteners, bleach-stable brighteners, nylon brighteners, and polyester brighteners, according to the substrate or purpose for which they are intended.

Cotton Brighteners

The most commonly used cotton brighteners, shown in Fig. 4, are bistriazinyl derivatives of 4,4′-diaminostilbene-2,2′-disulfonic acid. These so-called CC/DAS brighteners are prepared from 2 moles of cyanuric chloride (CC) and 1 mole of the disodium salt of diaminostilbene disulfonic acid (DAS). With the exception of Brightener DMDDEA, all are reaction products of 1 mole of CC/DAS with 2 moles of aniline (Brightener DMDDEA is the reaction product of 1 mole of CC/DAS and 2 moles of sulfanilic or metanilic acid).

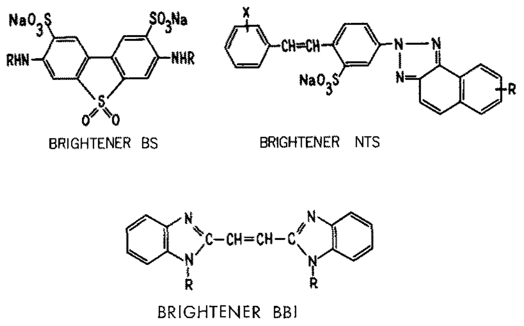

FIG. 5. Bleach-stable brighteners.

Other Brighteners

Fig. 5 shows typical structures of brighteners that are stable to chlorine bleach in the wash liquor. These are benzidine sulfone disulfonic acid (Brightener BS), naphthotriazolylstilbene sulfonic acid (Brightener NTS, R = H), and benzimidazolyl (Brightener BBI) derivatives.

The general structures of typical nylon and wool brighteners used are shown in Fig. 6. These are amino coumarin (Brightener AC) and diphenyl pyrazoline (Brightener DP) derivatives, none of which are stable to chlorine bleach.

The general structures of polyester brighteners that also have affinity for polyamide fibers are shown in Fig. 7. These brighteners are bisbenzoxazolyl (Brightener BBO), naphthoxazolyl (Brightener NOS), and naphthotriazolyl (Brightener NTSA) derivatives.

Activity of Brighteners

The active content of a brightener can be determined by comparing a sample of unknown strength with a reference sample of the same chemical structure and known strength (4). The chemical type of an unknown brightener must be determined before a comparison of strength can be made.

Because only a limited number of chemically different products are used by the U.S. detergent industry, the chemical type can usually be determined with a high degree of certainty by thin-layer chromatography, spot tests, wash tests, or by ultraviolet, excitation, and emission spectra.

Active-ingredient-content comparisons are usually based on optical density measurements, fluorescence measurements of highly dilute (1 ppm) brightener solutions, or fabric fluorescence obtained in wash tests by using stock solution.

The active content of a brightener does not yield

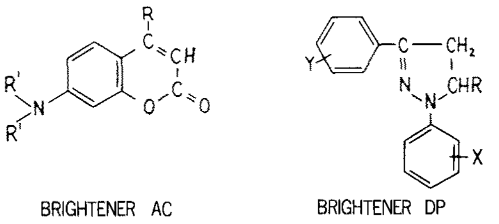

FIG. 6. Polyamide brighteners.

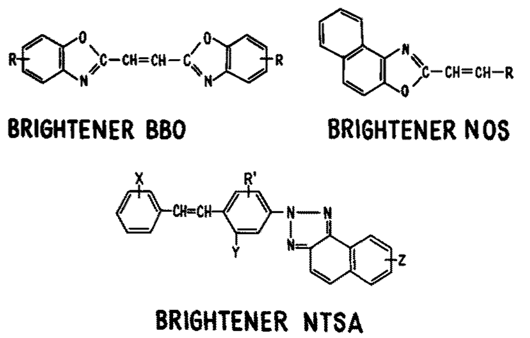

FIG. 7. Polyester and polyamide brighteners.

information on its performance properties. The performance of a brightener can only be evaluated by tests run under conditions which closely simulate use conditions.

Performance Properties

Selection of a brightener is commonly based on its performance per unit cost. The performance properties of a brightener are not only related to its chemical structure and to its activity but also to its physical form and purity. Consequently chemically equivalent brighteners of equal activity do not necessarily exhibit the same performance properties. It is important therefore, before different brighteners are compared for performance, to ascertain that the particular samples are of known composition. If the comparison is part of a selection process, the samples should be representative of the delivered materials.

A large number of performance properties are considered in selecting a brightener for a detergent. The relative importance assigned to the various properties depends largely on marketing considerations. Factors often considered are listed in Table II.

Incorporation

Besides being easy to incorporate in a detergent formulation, a brightener should be stable to processing conditions. The most severe conditions are probably those in which a detergent brightener is preslurried in a strong alkaline medium, added to the feed slurry, and spray-dried at high temperatures. Useful brighteners must not only be resistant to such conditions but also should be stable on storage in the product so that the latter will exhibit its full whitening power when used. Brighteners used in liquid laundry products must be compatible with the formulation, remain stable in the solution, and not cause separation or otherwise decrease the performance characteristics of the product.

TABLE II
Performance Properties

A. Incorporation	B. Detergent
Ease of incorporation	Detergent whitening or coloring
Stability during incorporation	Storage stability
Compatibility	
Toxicity	

C. In Wash Liquor

Brightener	Conditions
Solubility/Dispersibility	Surfactant
Rate of solution	pH
Affinity	Temperature
Exhaust rate	Inorganic electrolyte
Exhaust equilibrium	Agitation
Leveling	Detergent/fabric/liquor ratio
Build-up	Duration
	Hypochlorite stability

D. On Fabric

Whiteness	Fastness
Initially	Light
On build-up	Gas
Alone	Softeners
With other brighteners	Sours
	Perspiration
	Ironing
	Humidity
	Washing
	Ageing
	Metal ions

Detergent Whitening or Coloring

At the high brightener levels used today (0.3–0.5%), the effect of brighteners on the appearance of the detergent powder has become quite important. Some brighteners improve the whiteness of a detergent powder whereas others do not. Detergent brightening is generally related to the chemical structure, purity, and physical properties of the brightener, to brightener concentration, to other components in the formulation, and to the incorporation techniques used by the detergent producers. The whitening effect of some brighteners in anionic and nonionic detergent powders is shown in Table III.

The brightener should not change the shade of colored products. If a shade change does occur, it should be reproducible. In special cases, brighteners are used as colorants.

Brighteners in the Wash Liquor

Steps in Brightening Process. Detergent brighteners are introduced to the wash liquor with the laundering products, usually in powder form. To become effective, the brightener must dissolve or disperse in the liquor, Step 1, and then exhaust from the liquor onto the surface of the fiber substrate, Step 2. After deposition on the fiber surface, most brighteners will subsequently distribute themselves (migrate) throughout the fiber, Step 3.

Generally either Step 1 or Step 3 will govern the rate of brightening. The rate of Step 1 is related mainly to the chemical structure of the brightener and to its physical form in the detergent but also to the wash temperature and to the degree of agitation. The adsorption of the brightener molecule onto the fiber surface (Step 2) takes relatively little time. Step 3, the diffusion or migration of the brightener into the fiber, is slow because of mechanical obstructions and the restraining forces between the fiber and the brightener. The mechanism of brightener/fiber interaction depends on both the chemical structure of the brightener and on the fiber type.

a) *Cellulosic Fibers*—The CC/DAS brighteners behave like direct dyestuffs on cotton (1). The cellulosic fibers, being hydrophilic, swell in water, and the pores in the amorphous region grow to 15–30 Å in diameter, large enough to admit the brightener molecules. To achieve high affinity for cellulosic fibers, the brightener molecule should have several conjugated double bonds and aromatic nuclei of coplanar configuration. Of course, the latter is also a requisite for fluorescence of the molecules.

It can be seen from Fig. 8 that the *trans*-form of Brightener TA (and the other CC/DAS derivatives

TABLE III
Detergent Whitening

% Brightener	Whiteness (W) of Powder	
	Anionic	Nonionic
0.4% TA (fast)	113.3	140.4
0.4% TA (slow)	100.8	140.3
0.4% DM	100.9	135.7
0.1% NTS(R = H)	111.0	125.2
0.1% BBO	112.9	104.7
No brightener	82.9	90.2

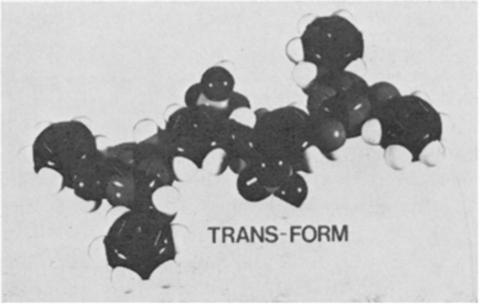

Fig. 8. Brightener TA, trans-form.

as well) fulfill the above requirements. How a "direct" type of brightener (DTB) is attached to the cellulosic chains (CE) is shown schematically in the upper part of Fig. 9.

Dry-cured, resin-treated Durable-Press cotton does not swell in water to the same extent as untreated cotton. Extensive cross-linking hinders the build-up of the regular CC/DAS brighteners (Fig. 9, lower part). Cotton, resin-treated and wet-cured in the swollen state, will allow a higher degree of brightener penetration.

b) *Synthetic Fibers*—Brightening of hydrophobic fibers, such as nylon, polyester, and acetate in an alkaline detergent liquor, takes place by a procedure similar to the dyeing of these fibers by dispersed dyestuffs (1).

Dispersed dyestuff molecules are relatively small in size and exhibit low solubility. Some investigators believe that the solid dyes dissolve in the solid fiber, others believe that the dyes penetrate into "canals" between the fiber molecules. A third group theorizes that the so-called water-insoluble dyes are, in reality, soluble to a small extent. The small amount of dissolved dye enters into, and is adsorbed by the fiber, permitting more dye to dissolve, etc.

Some synthetic fibers, for example, polyester, are extremely compact below the softening temperature. They do not swell to any significant extent in water, at least not at the temperatures below 150F employed in the U.S. home laundry. The effectiveness of currently available polyester brighteners, present in some consumer detergents, is therefore limited, especially on mass-brightened polyester (21).

Leveling. Fortunately Steps 2 and 3 (wash liquor/fiber surface/fiber interior), are two-way processes. Initially the brightener exhausts onto the fiber but unevenly. However a properly chosen brightener establishes an equilibrium between fiber and liquor. Part of the brightener returns to the liquor and re-exhausts back onto the fiber, gradually reducing uneven brightener distribution until, at the end of the wash cycle, a perfectly uniform brightening is obtained. A brightener like DMEA, which in alkaline detergent liquors has the ability to distribute itself evenly (Fig. 10), will give unlevel effects when applied in acid sour. At low pH this brightener has insufficient solubility to allow a fiber/liquor equilibrium and therefore stains the cotton fiber in unlevel fashion.

A brightener DMDDEA, with four sulfonate and two diethanolamino groups, has sufficient solubility even at low pH to give level effects and good buildup. The pH is only one of many factors that govern the distribution of a brightener between the fiber and the wash liquor.

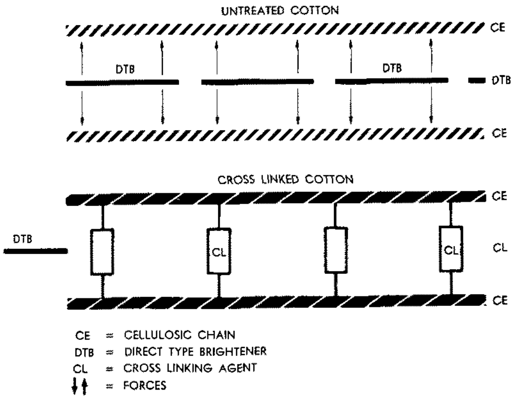

Fig. 9. Brightening of cotton.

Solubility and Solubility Rate. Although the solubility of the commonly used brighteners in a detergent wash liquor is relatively low, it is still high enough to allow a sufficient amount to dissolve (Step 1). The exhaust of brightener onto the fiber (Step 2) and migration into the fiber (Step 3) allow more brightener to dissolve in the liquor. It should be noted that the total concentration of brightener in the liquor of the modern American home laundry would be only 3–10 mg/liter even if all the brightener were in solution at one time. However differences in relative solubility of chemically different products are at least partly responsible for their degree of affinity for a substrate. Of course, the affinity depends also on the substrate type and wash-liquor conditions (Table II, Item C).

As has already been mentioned, the rate of solution (Step 1) of a brightener added to the wash liquor in a detergent powder is not only a function of the brightener's chemical structure but also depends on its physical form and the procedure used to incorporate it into the detergent powder. The rate of solution is often more important to the relative

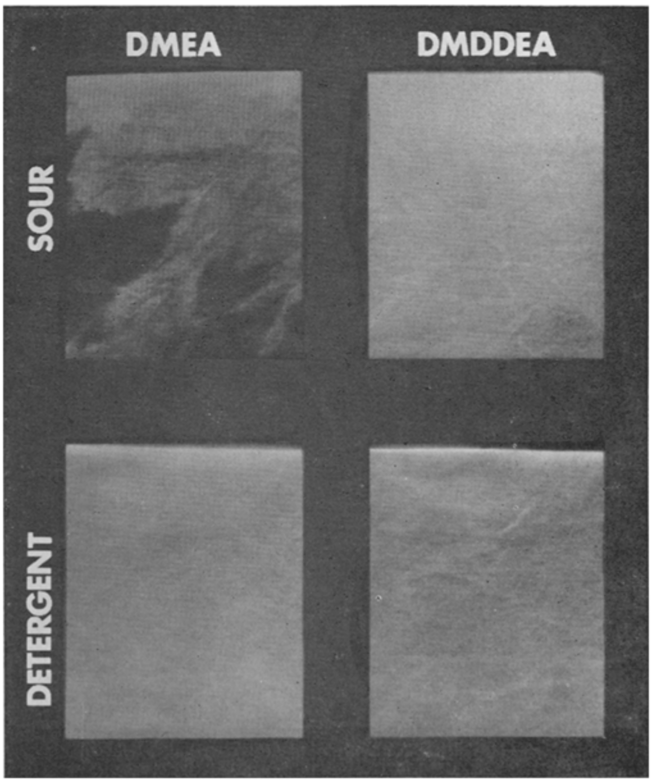

Fig. 10. Effectiveness of DMEA and DMDDEA.

performance of two chemically similar brighteners than the equilibrium solubilities of the products. If a brightener requires more time to dissolve and exhaust onto the fabric than the duration of the wash cycle (5–15 min in the United States), a large portion of it will simply go down the drain. Similarly, for water-insoluble products, both the degree and the rate of dispersion are important to brightener performance.

The effect of rate of solution on the performance of brighteners can easily be demonstrated in laboratory tests. Results of these and other tests, shown in the following tables, were obtained from wash tests in the Terg-O-Tometer and from measurements of washed fabrics on the Hunterlab Model D25 Color Difference Meter and the Lumetron Fluorometer (Photovolt Corporation, New York). Wash tests were run for 10 min at 80F, 130F, or 160F by using 20 g of cotton (C) or polyester (P), 600 ml of water, 1 g of anionic or nonionic built detergent, and brightener concentrations (full strength, on weight of detergent), as indicated.

Brighteners were added from stock solution or were incorporated in the detergent and added with the dry detergent powder. In the latter case, the detergent powder was predissolved for exactly 30 sec prior to the addition of fabrics. Bleach (200 ppm NaOCl), when used, was added to the wash liquor containing detergent and brightener, 20 sec or 3 min before the addition of fabrics. The standard conditions used (if not otherwise indicated) were 130F, 20 g of cotton, and 1 g of anionic detergent-containing brightener. The W (=whiteness) values shown were calculated from Hunter L, a, and b values by using the $W = L + 3a - 3b$ function. The reported F values are Lumetron fluorescence units. The relation between W values or F values and visually observed whiteness has already been discussed. These instrumental values (W and F) are useful expressions in describing brightener performance. Their true meaning and limitations must however be borne in mind.

Table IV shows that brightener performance can be affected by the method of brightener addition to the wash liquor. For example, Brightener TA (slow rate of solution) is much less effective on cotton when added with the detergent powder in solid form than when added predissolved from stock solution. Brightener TA (fast rate of solution) and Brightener DM however build up to the same fabric fluorescence regardless of the method of brightener addition. Brightener NTS, with a fast rate of solution, gives approximately the same effect independent of method. Brightener BBO, a water-insoluble product, exhibits poorer build-up on polyester from a detergent powder than if it is predissolved before adding.

Affinity and Exhaust. The degree of exhaust (Step 2) of a brightener onto a substrate is dependent on wash-liquor conditions. Under a selected set of these conditions and with sufficient time, an exhaust equilibrium will be reached. Ideally, at equilibrium, 90–95% of the brightener should be on the fabric and the rest in the bath to permit leveling. However the short wash-cycles used in this country do not always allow Step 2 and Step 3 to reach equilibrium. Sometimes less than 50% of the total brightener is found on the cloth. In practice, the distribution of brightener among detergent powder, wash liquor, fiber surface, and fiber interior is not a simple phenomenon. Usually the detergent contains a combination of brighteners, each with a different degree of affinity for the various fiber types in a mixed wash load; further complications arise from the presence of brighteners already in the fibers, brighteners which may, according to the reversible Steps 2 and 3, be transferred to the wash liquor.

TABLE IV

Method of Brightener Addition

% Brightener	Substrate	With detergent powder	From stock solution
		F	F
0.4% TA (slow)	C	327	400
0.4% TA (fast)	C	403	401
0.4% DM	C	407	403
0.1% NTS	C	299	303
No brightener	C	20	20
0.1% BBO	P	122	179
No brightener	P	10	10

Wash-Liquor Conditions

Surfactant. Brighteners TA and NTS, with good affinity for cotton in a built anionic detergent, are less effective in nonionic systems. A comparison of the CC/DAS brighteners indicates a relation between the polarity of the substituents on the triazine ring and their affinity for cotton in a polyethoxylated alkylphenol type nonionic formulation (22). Generally the affinity increases with increasing solubility of the brightener, and CC/DAS brighteners of low solubility are kept in the bath by the nonionic surfactant.

Brighteners like DM, DMEA, and DDEA with better solubility are effective in both anionic and nonionic systems. A water-insoluble brightener like NTSA however is more effective in nonionic systems (on polyester) than in anionic detergents. The distribution of brighteners between the aqueous phase and the fiber is, in other words, affected by the type (or types) of surfactants in the wash liquor.

Brightener performance in a typical anionic and nonionic built detergent is compared in Table V.

pH. Changes in pH of the wash liquor can cause changes in the "affinity" of the brightener for the aqueous phase and can also alter its distribution between liquor and fiber. Changes in pH also influence the degree of swelling of the fiber and leveling properties of the brightener. Fig. 10 shows that the effectiveness of DMDDEA is essentially independent of the pH of the wash bath. The buildup of DMEA is inferior to that of DMDDEA in acid sours but is better in alkaline detergents. In other words, the highly soluble CC/DAS brightener is equally effective at high and low pH values, but its affinity for cotton is lower in an alkaline bath than the less soluble DDEA, DMEA, DM, and TA. The latter products, having a fairly low solubility in an alkaline liquor, become partly insoluble in acid sours. Contrary to the low solubility CC/DAS types, brightener NTS is almost equally effective at low and high pH values.

Temperature. The cotton affinity of most of the commonly used CC/DAS derivatives is not significantly affected by temperature changes between 80–

TABLE V

Effect of Surfactant

% Brightener	Substrate	Anionic	Nonionic
		W	W
0.4% TA (fast)	C	124.9	113.3
0.4% DM	C	124.9	124.4
0.1% NTS	C	107.2	104.7
No brightener	C	91.5	91.5
0.1% BBO	P	91.3	88.5
No brightener	P	83.5	83.5

TABLE VI

Effect of Temperature

% Brightener	Sub-strate	Wash Temperature		
		80F	130F	160F
		W	W	W
0.4% TA (slow)	C	100.7	114.8	124.7
0.4% DM	C	122.6	126.7	127.7
0.1% NTS	C	107.3	108.7	107.7
No brightener	C	90.3	91.3	94.7
0.1% BBO	P	86.9	91.3	95.7
No brightener	P	....	83.5	....

TABLE VIII

Effect of Temperature on Bleach Stability
(3 Minutes of Exposure)

% Brightener	Wash Temperature					
	80F		130F		160F	
	W	F	W	F	W	F
0.4% TA (slow)	100.1	99	105.8	147	104.1	139
0.4% TA (fast)	....	......	99.3	98	....	......
0.4% DM	119.6	242	101.1	126	93.8	37
No brightener	93.1	20	93.1	......	94.3	......

140F (the range of U.S. home-laundering temperatures) if the brighteners are added in predissolved form to the wash liquor. But, if added in a solid form with the detergent powder, the rate of solution (and hypochlorite bleach stability) of some brighteners is strongly affected by the wash temperature.

The effectiveness of slow rate of solution products such as TA (Table VI) increases with increasing temperatures. Fast-rate-of-solution products are only slightly affected (DM) or not affected (NTS) by the wash temperature. Brightener BBO becomes more effective at higher temperatures because polyester fiber is easier to penetrate when it becomes softer.

It is also known that the same brightener will exhibit a slightly different hue of white as a function of the application temperature. The reasons for differences in hue are probably related to Step 3, the distribution or migration of the brightener within the fiber.

Inorganic Electrolyte. The solubility and therefore the distribution between wash liquor and substrates of some brighteners is affected by the concentration of inorganic electrolyte in the liquor. Brighteners that require a certain concentration of electrolyte to exhaust are not suited for electrolyte-free systems. Yet high concentrations of electrolyte may force certain brighteners out of solution, making the product an ineffective precipitate.

Agitation. The amount of mechanical work applied during washing will increase the rate of solution of a brightener and also influence its distribution between wash liquor and cloth. High agitation is desirable, of course.

Brightener/Detergent/Fabric/Liquor Ratio. Variations in ratio will affect the performance of brighteners. For example, at a constant detergent/fabric ratio, a decrease in fabric/liquor ratio will affect the rate of solution. If the CC/DAS brighteners are already dissolved in the liquor, changes in the fabric/liquor ratios commonly used in the home laundry will not affect performance significantly.

Duration. Both Step 1 and Step 3 are relatively slow processes, the rates of which depend on the brighteners used. In other words, two products might perform equally well in wash cycles of 20-minutes duration, yet in a shorter cycle one of these brighteners could be much inferior to the other.

Hypochlorite Stability. Of all laundering aids commonly added to the wash liquor, only active chlorine products affect the stability of some brighteners. The extent of attack on the so-called bleach-unstable brighteners depends on their chemical structure, their rates of solution, amount of bleach used, timing and order of addition of all ingredients of the wash, temperature, etc.

The longer the brightener remains in the wash liquor in the presence of active chlorine, the more brightener will be destroyed. It is preferable therefore to delay the hypochlorite addition until most of the brightener is adsorbed on the substrate. Protected by the substrate, most bleach-unstable brighteners are not destroyed by hypochlorite.

Differences in stability to hypochlorite and dichloroisocyanurate bleaches exist even among the CC/DAS derivatives. This indicates that the bleach stability of these compounds is directly or indirectly related to the amine which is used for the reaction with the second reactive chlorine on the triazine ring. Brightener NTS, which has no secondary amine groups, is quite bleach-stable. Brighteners like BBO, NOS, and BBI, which are practically water-insoluble, also exhibit good bleach stability. An oxidation of these brighteners by $NaOCl$ is more difficult because the brighteners are not dissolved in the aqueous phase and are thus not as susceptible to attack by the bleach.

Two chemically equivalent brighteners may react differently to the same bleach, depending on the time required for the brightener to go into solution, the time spent in the aqueous phase, and the time it takes for the brightener to exhaust onto the fiber.

Differences in bleach stability of brighteners and the effect of exposure time are shown in Table VII. Because the bleach also can improve the whiteness of the substrate, W values reflect improvements in whiteness caused both by bleach and by the brightener. The F values indicate the amount of intact brightener exhausted onto the fabric. The brightener, of course, emits more efficiently, the whiter the substrate.

The reactivity of hypochlorite increases with increasing temperatures. Rate of solution (Step 1) and the rates of Step 2 and Step 3 are also temperature-dependent. For fast-rate-of-solution CC/DAS products, the bleach stability decreases with increasing temperatures (Table VIII). It is interesting to note however that the slow-rate-of-solution type TA

TABLE VII

Bleach Stability

% Brightener	Sub-strate	Exposure Time					
		No Bleach		20 Seconds		3 Minutes	
		W	F	W	F	W	F
0.4% TA (fast)	C	124.9	403	104.0	174	99.3	98
0.4% DM	C	124.9	407	113.8	265	101.1	126
0.1% NTS	C	107.2	299	111.5	284	109.1	270
No brightener	C	91.5	20	93.2	......	93.4	......
0.1% BBO	P	91.3	122	90.8	119	91.1	113
No brightener	P	83.5	10	......	......	85.0	......

TABLE IX

Effect of Surfactant on Bleach Stability
(3 Minutes of Exposure)

% Brightener	Substrate	Anionic	Nonionic
		W	W
0.4% TA (fast)	C	99.3	100.6
0.4% DM	C	101.1	104.2
0.1% NTS	C	109.1	103.6
No brightener	C	93.4	93.4
0.1% BBO	P	91.1	88.5
No brightener	P	85.0	85.0

TABLE X

Gas-Fading

Brightener	Whiteness (W)	
	Before exposure	Exposure 1 cycle
NTS	102.4	102.1
BBI	103.0	87.8

brightener is more effective at 130F and 160F than at 80F, also that the slow TA type exhibits better whiteness than DM at the higher temperatures. Normally DM is regarded as being more bleach-stable than TA.

At the higher temperatures in the case of the slow-rate-of-solution TA, the hypochlorite bleach reacts with other components in the wash liquor and becomes deactivated before all the TA (slow) has gone into solution. During the last minutes of the wash cycle, the brightener deposits on the fabric and finally exhibits a higher fluorescence than the fast rate of solution products.

The bleach stability of a brightener is to some extent affected by the type of surfactant used (Table IX). Impurities in brighteners may also affect bleach stability. It is important that decomposition products formed on exposure to bleach do not exhaust onto the fabrics to cause discoloration.

Brightener on Fabric

Whiteness

Some investigators rate brightener performance after the first application as the most important; others judge the brightener on its effectiveness after repeated washings. Because brighteners frequently are used in combinations, the contribution of the "package" is often evaluated rather than the single components. Also, the over-all effect on a mixed, soiled, prebrightened wash load may be considered a more realistic measure than the effect of a single brightener on a clean, unbrightened, one-fiber substrate.

Fastness

Establishing a distinction between "stability" and "fastness" of brighteners has been suggested. Stability is related to conditions affecting the brightener before it is on the substrate whereas fastness is related to the behavior of the brightener after deposition on the fiber. "Fastness" will be used loosely, to describe that property of a brightener relating to its effectiveness on exposure to all types of treatments.

Detergent brighteners used for cotton have sufficient fastness to remain effective for at least one day of light exposure. For example, the fluorescence value (F) of cotton treated with 0.3% brightener DM was reduced from 258 to 186 on exposure to 500 langleys of sunlight (an average day of light exposure in the New York, N.Y., area is equivalent to approximately 375 langleys). Washing after one day's wear, usual practice in the United States, therefore replaces the degraded brightener.

TABLE XI

Typical Brightener Levels
(U.S. Detergents)

Product	Brightener[a]					
	DM	DDEA	TA	NTS-(R=H)	BBO	NOS
Detergent A	0.50%	....	....	0.04%	....	....
Detergent B	0.20%	....	....	0.10%	....	....
Detergent C	0.40%	....	....	0.03%	0.02%	....
Detergent D	0.20%	0.08%	....	......	0.02%	....
Detergent E	0.30%	....	....	0.04%	0.02%	....
Detergent F	....	0.20%	....	0.10%	....	0.03%
Detergent G	0.46%	....	....	0.09%	....	....

[a] Full strength.

Fading of brighteners is considered important only when discoloration occurs. Most synthetic fiber brighteners exhibit better light fastness than cotton brighteners. Some brighteners discolor on exposure to atmospheric gases. Fastness of brighteners to gas-fading can be tested with an AATCC gas-fading apparatus (Standard Test Method AATCC 23–1962 or 75–1956). Changes in whiteness on exposure can be recorded. Gas-fading properties of brightener NTS and BBI are compared in Table X. Cotton swatches were exposed for one cycle (12 hr) in the AATCC gas-fading chamber.

There are still other "exposures" to consider. The use of cationic softeners in the rinse bath can "quench" some of the detergent brightening (23). Some brighteners discolor on exposure to acids, such as sours in commercial laundries, to deodorants, and to perspiration. Brighteners can also be affected by ironing, humidity, and the presence of trace metals on the substrate. Brighteners on fabrics, upon laundering, will, to some extent, bleed into the liquor where they may be affected by hypochlorite bleach if present.

Brighteners should therefore be tested for fastness by measuring fabric fluorescence and whiteness before and after exposure to simulated conditions in the laboratory.

Brightener Usage

Because commercial detergents vary in their composition and are frequently designed for a specific type of laundry, and because formulators assign a different degree of importance to the various properties, brightener systems do vary. Typical brightener systems used in American heavy-duty detergents in early 1967 are shown in Table XI.

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