Fluorescent Agents for Detergents

H. W. ZUSSMAN, Geigy Industrial Chemical Div., Ardsley, New York

OPTICAL BRIGHTENERS currently constitute 0.1–0.2% of home laundry detergents. Although brighteners may be considered minor ingredients, it would not be presumptuous to claim that brighteners are indispensable detergent ingredients. Largely because most laundry detergents do a creditable cleaning job, the housewife has become sensitive to brightener effects; she probably can detect an increase in brightener content more readily than any other formulation change except possibly product color or odor. The housewife appreciates whiteness and brightness. A recent consumer survey (1), in which one thousand housewives of working class background were questioned on how they judged performance of laundry products, indicates that whiteness (in white laundry) and brightness (in colored laundry) are considered more important than clean appearance.

Detergent producers are aware of this; if they didn't mold this attitude, they have fostered it in their advertising. Yet there is evidence that the value the consumer attaches to brighteners is not entirely the result of consumer education. Brightener is used almost universally and in increasing concentration; this applies not only to North America and Europe but to many parts of the world unfamiliar with American marketing techniques.

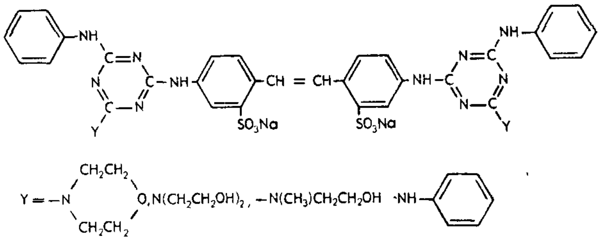
The Principle

The principle on which brighteners work is simple. A white fabric exposed to sunlight reflects almost completely both the visible component of sunlight and the ultraviolet component, about five per cent of the total incident solar energy. The human eye does not respond to this ultraviolet light. A fluorescent compound applied to the fabric, when excited by ultraviolet radiation, will convert this invisible radiation to visible; this the eye sees as added brightness. If the fluorescence is of suitable wavelength, it will mask discoloration in the fabric, making it appear whiter.

This concept and its application were appreciated more than 35 years ago. As frequently happens in the history of technology, commercial development was slow and indirect. About 1930, B. Wendt, then a chemist at the Agfa photographic film plant at Wolfen (now in East Germany, and still making brighteners) was asked to develop an ultraviolet absorber for incorporation in cellophane wrappers to retard light catalyzed rancidity in cookies and similar foods. The compound developed for this purpose was sodium dibenzoyl 4,4′ diaminostilbene 2,2′ disulfonate. The patent subsequently issued makes no mention of brightening effect; this apparently was noted when the compound was applied to paper intended for packaging butter. According to Dr. Wendt (2), the first commercial application of the brightening effect occurred about 1940 at the rayon plant in Wolfen; the brightener was incorporated in the viscose. Not until after the war was brightener added to soaps to whiten laundry.

Interest in brightener chemistry has spawned hundreds of patents during the past two decades. While thousands of compounds have been described, these are mainly variations on a few basic themes.

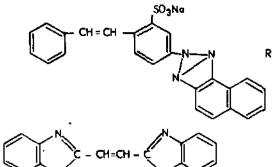
The most important "workhorse" brighteners in use today are indicated by:

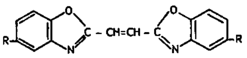


I II III IV

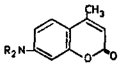
These products are all sensitive to chlorine bleach while in the dissolved state; they all have excellent cotton substantivity. The tetra-anilino derivative (IV) exhibits nylon substantivity as well and, for this reason probably, is the most widely used of the group. Together, this group accounts for approximately 70% of detergent brightener tonnage.

V



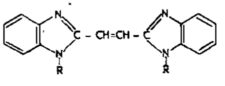


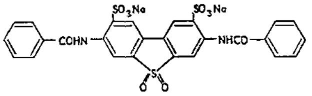
VI



VIII

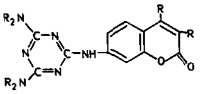
VII

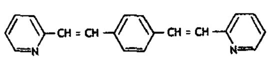


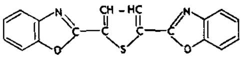


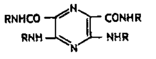
IX

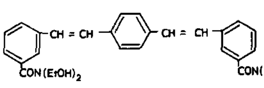
A second group includes other brighteners in common use. The most important of this group is the "all purpose" naphthyltriazole stilbene monosulfonate (V), which has good stability to hypochlorite in addition to multi-fiber substantivity. The ethylene bisbenzimidazole (VII) and ethylene bisbenzoxazole (VI) types are in the same general category. Customarily, hypochlorite stable brighteners of this type are used in combination with "workhorse" brighteners. Dialkylaminocoumarins (VII) brighten nylon, acetate and wool, but not cotton; poor bleach stability limits this type of product to fine fabric washing formulations. The sulfone (IX) is substantive to cotton only, but has exceptional stability to chlorine. Worth referring to, also, are methylumbelliferone and sulfonaphthortriazole stilbene monosulfonate, for brightening white and pastel toilet soaps.

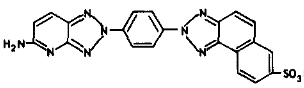












A third group shows some of the more unusual chemical structures referred to in the very recent patent literature. Not all of these are necessarily useful for detergents. Brighteners are also used extensively in paper, textile finishing, plastics, waxes, synthetic fibers.

The evaluation of brighteners for detergents is now on a reasonably sound basis, but is by no means un-

TABLE I

Fabric substantivity spectrum
Strength
Shade
Buildup
Preference

Excitation, emission spectra
Solubility
Characterization
Toxicity

Surfactant effects
pH
Dispersion, compatibility
Solution rate
Chemical stability
Detergent discoloration

Hypochlorite
Exhaustion rate
Equilibrium exhaustion
Temperature
Mechanical work
Levelling
Mixed load effects
Detergent:fabric:water ratio

Water rinse
Cationic
Light exposure (wet)
Gas drier
Ironing

Light exposure (dry)
Gas fading
Humidity
Spotting
Laundry sour
Storage
Tensile strength

complicated. Most of the elements of performance which must be considered in evaluation are listed in Table I. Even when the performance characteristics of a brightener are defined, the problem of weighing these characteristics remains. Consider two brighteners, otherwise equivalent, one of which has marginally better bleach stability, and the other, better light stability (on the fabric) and better brightening action on resin treated cotton. How does one choose between the two products? In the final analysis, the various elements of performance must be weighed against the objectives of the finished formulation. Since many of the performance elements listed in Table I have been reviewed elsewhere (3), only a few special subjects will be discussed here.

Determination of Strength

At the heart of the evaluation problem is the determination of "strength." This is not particularly difficult when different formulations of the same brightener are compared, or where different brighteners of the same hue are involved. Where there are qualitative differences in fluorescences, consumer preference must be determined. The consumer reaction is based on an integrated psychological response to hue and light intensity. Since these modalities may also be measured instrumentally, there is a strong temptation to rely on nonsubjective, physical evaluation techniques. This can be dangerous. Two instruments used in the Geigy laboratories are the Lumetron (Photovolt, N.Y.) and the Farrand reflectance spectrofluorimeter (Farrand Optical, N.Y.). The Lumetron measures emission of total visible light reflected from a fabric sample excited with 366 mμ radiation. The spectrofluorimeter, fitted with two diffraction grating monochromators, permits the excitation of a sample with any desired wavelength selected from a Xenon lamp spectrum; excitation as well as emission spectra may be obtained. If the first monochromator is bypassed, sunlight, Xenon lamp light or indoor light may be used for excitation. The response characteristics of the phototubes used with these instruments are compared (adjusted to equal height) with the sensitivity curve of the human eye in Figure 1. It should be noted that the human eye is more sensitive to greenish light than to bluish light of equal energy content. Greenish fluorescence, which might be expected to appear brighter to the human eye, is less effective than bluish fluorescence in masking yellow discoloration; it is apparently less pleasing psychologically as well.

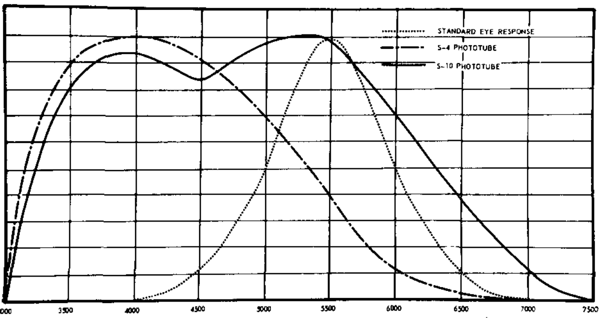


FIG. 1. Spectral response characteristics of light adapted human eye and commonly used phototubes.

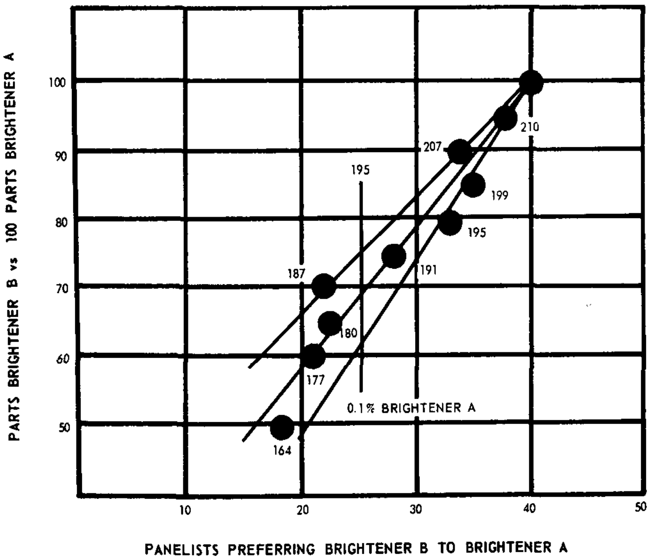


FIG. 2. Panel preference test on cotton fabrics treated with varying levels of test brightener vs. standard brightener.

A comparison of the brightening effect of two fluorescers by the two instruments and by a 50-member panel may be of interest. Experienced observers can detect 5% differences in brightener strength without difficulty, but because such observers develop prejudices for the hue preferred by the test operator, untrained (female) panels are employed.

A series of cotton fabrics is prepared under standard washing conditions using a single level of the standard brightener A (at 0.1% in a detergent) and various levels (0.06, 0.07 . . . 0.12% for example) of the test brightener B. Each of the test fabrics is submitted separately to the panelist, along with the standard, and an expression of preference is solicited; the comparison is limited to two fabrics at any time, ideally at noon under north light from a clear or only slightly cloudy sky. Each point in Figure 2

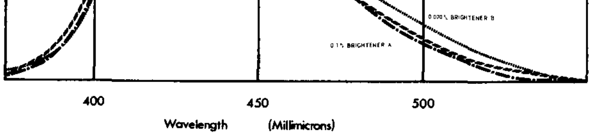


FIG. 3. Emission spectra of cotton fabrics treated with 0.065 and 0.070% Brightener B compared with 0.10% Brightener A.

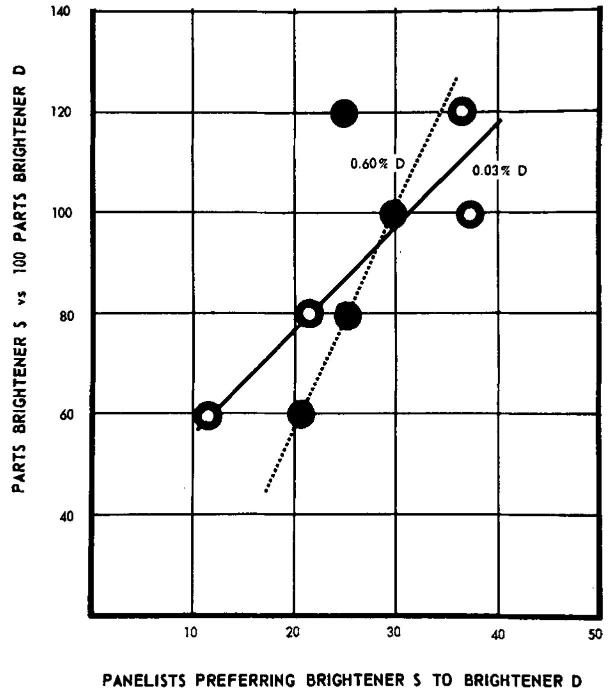


FIG. 4. Panel preference test on brighteners at 0.03% and 0.60% in detergents, applied to nylon.

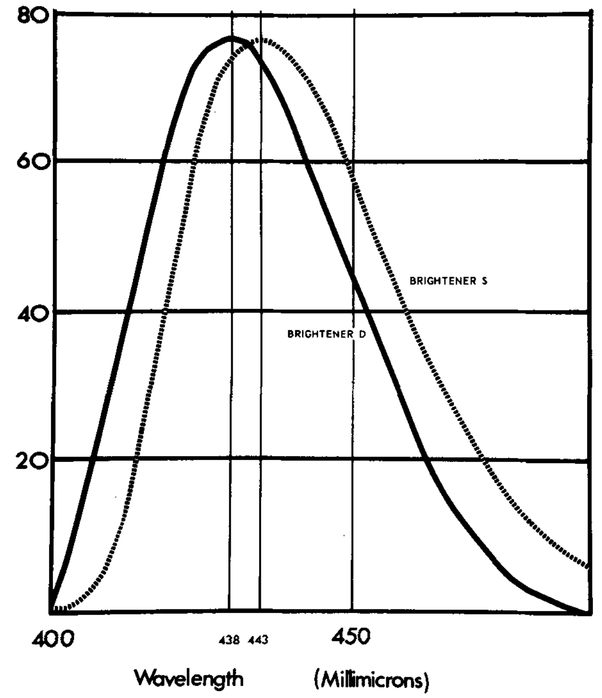


FIG. 5. Emission spectra of Brighteners D and S on nylon, corrected to equal height to show shade difference.

denotes the preference for a specific test sample vs. the standard; the figure beside each point is the Lumetron fluorescence reading for the particular test sample. The Lumetron rates 100 parts brightener A equal to 80 parts brightener B. According to the preference panel, 69 parts brightener B are equal to 100 parts brightener A. Interestingly, a straight line may be drawn through a plot of the Lumetron readings; the match of the curve to the preference data is less satisfactory. The emission spectra for fabrics treated with 0.1% brightener A and with 0.065% and 0.070% brightener B are shown in Figure 3, confirming the preference panel results in a general way. Although the emission spectra of the two brighteners appear very similar, trained observers have no difficulty detecting a shade difference, brightener A being considered redder (e.g., less green) than brightener B.

Another preference study, of brighteners S and D on nylon, is summarized in Figure 4. The standard D is compared at two different levels, 0.03 and 0.60% in detergent, against various corresponding levels of the test brightener S. The emission spectra of these two brighteners are quite different (Fig. 5), with a 5 mμ difference between peaks. The Lumetron is of no value in making a comparison of these compounds. It might be noted that the panel's discrimination—which is related to the slope of the curve—is not sensitive to changes in hue, comparing the results obtained in the comparison of A and B, and in the comparison of S and D at the low level. As might be expected, discrimination is less in the high level comparison of S and D than in the low level comparison.

Multi-Fiber Brightening

Ideally, a laundry detergent should brighten all washable fibers; no such formulation has been achieved practically. The diaminostilbene disulfonate brighteners show about 80% exhaustion on cotton; they have no affinity for cellulose acetate. Viscose rayon and wash 'n' wear cotton usually show lowered affinity for these brighteners. This is illustrated in Table II. Anionic detergents were formulated with four different bistriazinyl diaminostilbene disulfonates, concentrations adjusted to produce equal whitening of untreated cotton. The detergent/brightener formulations were then tested on three common resin treated cottons at 120F. Since lower washing temperatures are recommended for such fabrics, the tests were repeated at 80F.

While nylon presents no problem, polyester—even in cotton blends—is still a challenge; so are acrylic and spandex fibers, with polypropylene still to make its appearance. The development of a brightener for any one of these fibers is a formidable task. The development of a single brightener suitable for all fibers is highly improbable. It is unlikely that a brightener will distribute equally among a variety of fibers in a mixed load of varying composition. Optimum conditions for brightening one fiber will not necessarily be satisfactory for another fiber. It is unlikely that the shade characteristics of one compound will be satisfactory for all fibers. Figure 6 compares the emission spectra of a single brightener in three different polymer films. The nylon and cellulose acetate used were clear moulding grade resins; the acrylic film was produced from commercial fiber. The lowered fluorescence in acrylic is probably due to titanium dioxide from the original fiber; rutile TiO_2 absorbs strongly in the ultraviolet range and has a quenching effect on the brightener. The shift in emission of the brightener in acetate was unexpected

TABLE II
Fluorescence of DASS/CC Brighteners on Resin Treated Cotton; Application from Anionic Detergent

Y	Untreated	Urea-form.	Triazone	Triazine
	%			120F
$N(CH_3)CH_2CH_2OH$	263	239	244	153
NHC_6H_5	262	251	246	179
$N(CH_2CH_2OH)_2$	264	241	252	151
$N(CH_2CH_2)_2O$	262	232	248	149
				80F
$N(CH_3)CH_2CH_2OH$	257	233	244	151
NHC_6H_5	258	244	232	166
$N(CH_2CH_2OH)_2$	258	232	242	147
$N(CH_2CH_2)_2O$	259	221	241	145

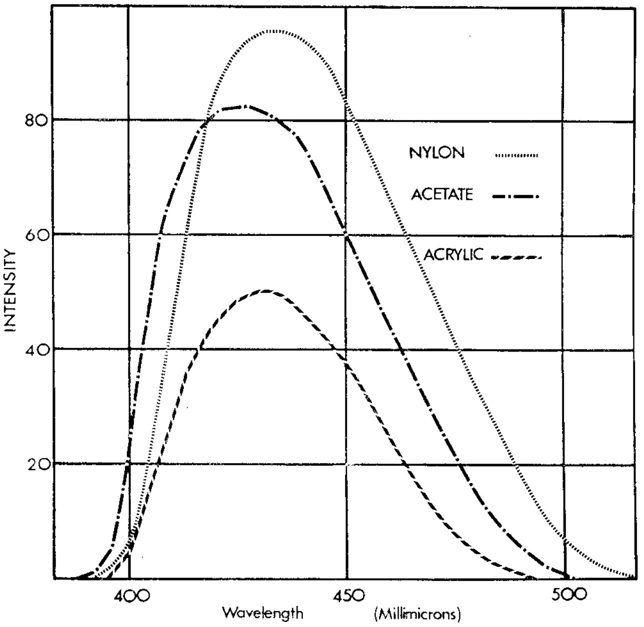


FIG. 6. Emission spectra of plastic films of equal thickness, containing the same concentration of brightener.

since the excitation spectra of the brightener in all three polymers peaked at the same wavelength. Likewise, the increasing interest in organic ultraviolet absorbers for synthetic fibers suggests a further complication of the detergent brightener problem. On the other hand, the fiber producer's increasing reliance on stabilizers and brighteners of high fastness to improve service and maintenance characteristics may possibly alleviate the problem.

Effect of Chlorine on Brighteners

Consumption of chlorine for home laundry use is increasing at a faster rate than consumption of laundry detergent. This is reflected to some extent in the high percentage of brightener V used in combination with diaminostilbene disulfonate compounds. The latter are stable to hypochlorite once they are adsorbed on cotton but are rapidly destroyed in solution. In some cases, a protective effect by the detergent is noted. In Figure 7, fluorescence values on cotton are plotted against time of exposure of detergent/brightener to hypochlorite before addition of the fabric. The two brighteners X and Y are both diaminostilbene disulfonate types; both have equally poor bleach stability in anionic detergent and better stability in nonionic with Y showing an advantage over X. Figure 8 illustrates the effect of low temperature on bleach stability. This is of interest in connection with cold water washing. In this instance, the improved stability of the brightener at low temperature is due to the retarded decomposition of the hypochlorite.

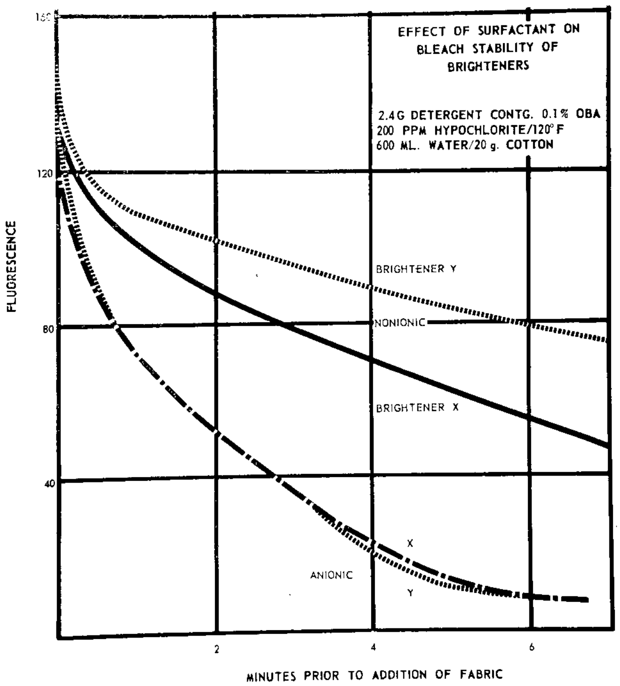


FIG. 7. Effect of surfactant on hypochlorite stability of Brighteners X and Y in solution.

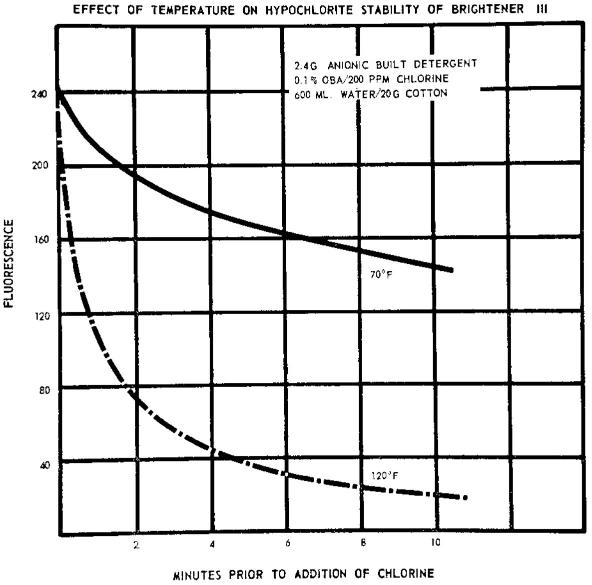


FIG. 8. Effect of temperature on hypochlorite stability of Brightener III.

Biological Aspects

In view of the current interest in environmental safety, a few comments regarding brighteners may be apropos.

Brighteners do not affect the appearance of water (as normally viewed), nor the taste, at 1 ppm. Brightener concentration in wash water drained from a washing machine after a complete cycle is ca. 0.1 ppm; if the water is reused for a second laundry load, the brightener concentration is reduced to 0.01 ppm. Brightener is adsorbed on paper and on organic soils but not on sand or clay. It is unlikely, in any event, that brightener content in river water or at water treatment plants would run as high as one part per billion even under unusual circumstances. Brighteners have no detrimental effect on bacteria. Finally, the recent reports of Snyder (4), Neukomm (5), Glashoff (6) and coworkers indicate that brighteners now in general use are not hazardous.

ACKNOWLEDGMENTS

This paper based on work by the Customer Service Dept., Geigy Industrial Chemicals, and in particular from L. Wigdor, F. Noonan, Z. Steinert, and R. Rau.

REFERENCES

1. MacFadden-Bartell Corp., New York, N. Y.
2. Wendt, B., American Photocopy, Evanston, Ill., personal communication.
3. Zussman, H. W., W. Lennon, and W. Tobin, Soap, Chem. Specialties, *32*, 35 (1956).
4. Snyder, F. H., D. Opdyke, and H. L. Rubenkoenig, Toxicol. Appl. Pharmacol., *5*, 176 (1963).
5. Neukomm, S., M. deTrey, Med. Exptl., *4*, 298 (1961).
6. Glashoff, E., W. Stegmann, and E. Schroder, Seifen, Fette, Seifen Anstrichmittel, *65*, 42 (1963).