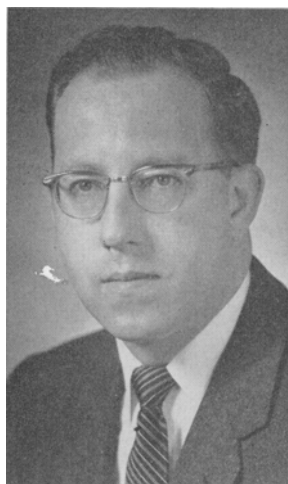27. Quimby, O. T., J. Phys. Chem., 58, 603–618 (1954).
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Optical Bleaches in Soaps and Detergents

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A GERMAN TEXTILE CHEMIST named Krais (1) demonstrated in 1929 that incompletely bleached linen could be made to appear much whiter by immersing it in an aqueous solution of aesculin and drying. The solution of aesculin was colorless but was highly fluorescent. This experiment proved Krais' theory that whitening of linen can be brought about by fluorescent blue light compensating for the blue light absorbed by the yellow contaminants in linen. Aesculin is a glucoside and can be found in the bark of the horse chestnut tree. The optically effective part of the molecule is 6,7-dihydroxy coumarin. This coumarin has no affinity for cellulosic fibers and was mechanically deposited in the soaking operation. A simple wash or rinse removed it from the fabric. It therefore was of little commercial value.

F. G. Villaume

In 1937 Imperial Chemical Industries obtained a patent (2) in which the use of N,N'-diacyl derivatives of 4,4'-diaminostilbene-2,2'-disulfonic acid for treating textile fibers is described. The patent mentions that such treated materials fluoresce under ultraviolet radiation, but there is no mention of a whitening effect being observed. About this same time I. G. Farben investigated the use of colorless, ultraviolet-absorbing materials as protective agents against deterioration by light, particularly by incorporation in wrapping paper. Some of the compounds studied were N,N'-bis-triazinyl derivatives of diaminostilbene (3), but again no indication was given of their potential value as whitening agents for textiles.

It was soon observed however that some of these compounds had excellent affinity for cellulosic material and produced a whitening effect. Subsequently I. G. Farben started to market several of these products, but further development was interrupted by World War II. The first products of this type were Blancophor B and Blancophor R.

After World War II an intense effort developed in the United States to exploit products of this type, particularly in soaps and detergents used for laundering. Research programs were initiated by the major soap companies and several of the dyestuff manufacturers. In September 1948 one of the major soap companies in the United States, Lever Brothers Company, announced that it had a whitening agent in its soap product. Five weeks later a second major soap company, The Procter and Gamble Company, made a similar announcement. Today it is difficult to find a soap or detergent recommended for washing cotton which does not contain an optical bleach.

Chemical Structure of Brighteners

What are optical bleaches (also referred to as brighteners, whitening agents, and fluorescent bleaches)? They can be classified as dyes if we define a dye as a substance that is able to affix itself to a textile fabric and influence the apparent color of the fabric. When material dyed with a nonfluorescent substance is placed in daylight or artificial white light, it will reflect part of the light striking it and will absorb part of it. The reflected light is perceived as color. The absorbed light is converted to longer wavelengths (infrared) and radiated as heat. With a brightener no significant visible light is absorbed. Rather, invisible ultraviolet energy is absorbed, converted to longer wavelengths, and emitted as visible blue light.

For a structure to be fluorescent, it seems that there must exist a conjugated double bond system as, for example, in the stilbene molecule (Figure 1). The stilbene nucleus is found in a number of the commercial brighteners. The electrons which hold the atoms together in a molecule are called bond or *sigma* electrons (4). Since the carbon atoms in the stilbene molecule need only three of their four valence electrons in the formation of *sigma* bonds, there remain free electrons in the molecule. These are the so-called *pi* electrons, the energy level of which can be changed easily by small forces such as light. In the lower diagram of Figure 1 the *pi* electrons are illustrated by asterisks and the *sigma* bonds by lines. Ultraviolet radiation can excite the *pi* electrons to a higher en-
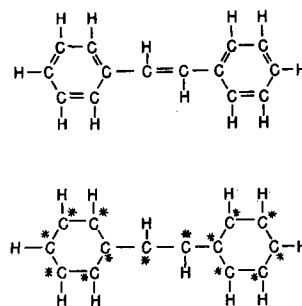

FIG. 1. Stilbene.

ergy level. When these electrons return to their original energy level, part of the light absorbed is emitted at longer wavelengths. In the case of optical bleaches the emission is in the visible blue region of the spectrum at about 440 mμ.

The spatial arrangement of a molecule also contributes to its fluorescence. Benzidine has little fluorescence; however when it is converted to benzidine sulfone, a planar configuration results and it then has increased fluorescence. Planarity is also required for substantivity to cotton. Substituent groups, such as amino, alkoxy, hydroxyl, halogen, and sulfonic acid, contribute to the fluorescence and substantivity of optical bleaches.

Since the above only touches upon the structural aspects of brighteners, it will probably be of interest to many to read a more thorough discussion of this subject. Such is presented in a paper by R. S. Long (5) and a text by Diserens (6).

Optical Effect

Color is usually thought of in what the physicist would call subtractive terms: blue and yellow make green, red and green give black, etc. But this concept applies only to the mixing of colorants, such as dyes and pigments, the hues of which result from their light absorption characteristics. The other aspect of color is mixing of colored light, or additive color. Here the results are drastically different. Red and green make yellow or orange, depending on their proportions. The mixing of greatest relevance to this discussion though is blue and yellow, which produce white. Comparing the optical action of brighteners to that of bluings and chemical bleaches is probably the easiest way of understanding the principles that underlie this new bleaching method.

Figure 2 shows reflectance curves of bleached 80 x 80 cotton fabric and of magnesium oxide, which is commonly accepted as the standard for whiteness (7). The curve for the bleached cotton differs from that of magnesium oxide in two respects: it is lower and slopes downward from right to left. The curve being lower indicates that the fabric is darker than standard. A reflectance of zero, complete absorption of all visible light striking a material, would indicate black. Complete reflectance, no absorption, would indicate a pure white. The reason for the slope is that more of the light in the violet and blue region is absorbed than that in the yellow together with green and red, or conversely more yellow light is reflected and the fabric therefore appears yellow. Thus the curve being lower and sloping from right to left, indicates that the fabric is both darker and yellower than the magnesium oxide standard. In order to approach the standard in whiteness, the reflectance curve must be both flattened out and raised.

When a bluing, e.g., a blue dye or pigment, is applied to the bleached cotton, the reflectance curve that then results is represented by the dotted line B (Figure 3). Curve O represents the original fabric. It is seen that the bluing has tended to flatten out the curve by absorbing light in the yellow region and thereby has decreased the reflectance of yellow light; however it should be noted too that the over-all reflectance is now less. Thus the cloth appears less yellow but also somewhat darker.

With a brightener this is not the case. Instead of absorbing visible light, the brightener absorbs ultra-
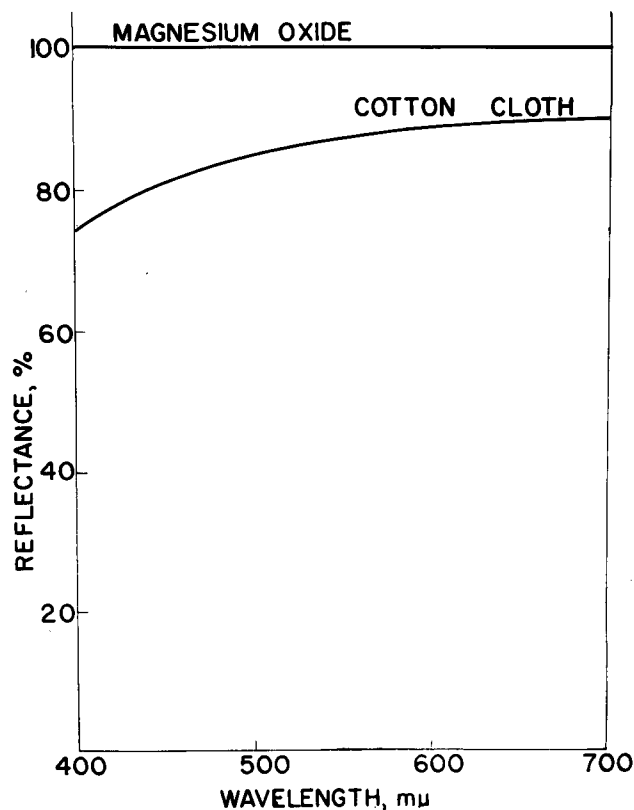

FIG. 2. Reflectance curves of magnesium oxide and bleached cotton cloth.

violet energy which is present in daylight, fluorescent, and incandescent light. It converts the otherwise unused invisible ultraviolet energy to visible blue light. Curve W (Figure 3) represents the apparent reflectance of the brightener-treated cotton. The brightener, by adding blue light instead of subtracting yellow light, makes the fabric not only less yellow but also less gray.

To make these effects more apparent the curves shown in Figure 3 were calculated in terms of yellowness and lightness values (7). Figure 4 shows the colors of the untreated cloth, the cloth treated with bluing, the cloth treated with brightener, and magnesium oxide plotted on a diagram with yellowness as one axis and lightness as the other. The units are such that one unit change of yellowness is equal visually to one unit change in lightness. It is seen that the bluing produces almost as much darkening of the cloth as it decreases the yellowness whereas the optical bleach lightens the cloth slightly while it decreases yellowness.

With a chemical bleach there is no darkening of the fabric. It makes a fabric less yellow and brighter by destroying or rendering colorless the substances in a fiber that absorb blue light; however there is a limit to the amount of bleaching a fiber will tolerate and after a certain point the fiber itself is likely to be tendered. Even after the maximum whiteness attainable by this method has been realized, it is still possble to increase the whiteness further by the addition of a brightener.

Application

In the laundry field brighteners are used in soaps, detergents, bleaches, bluings, fabric softeners, and
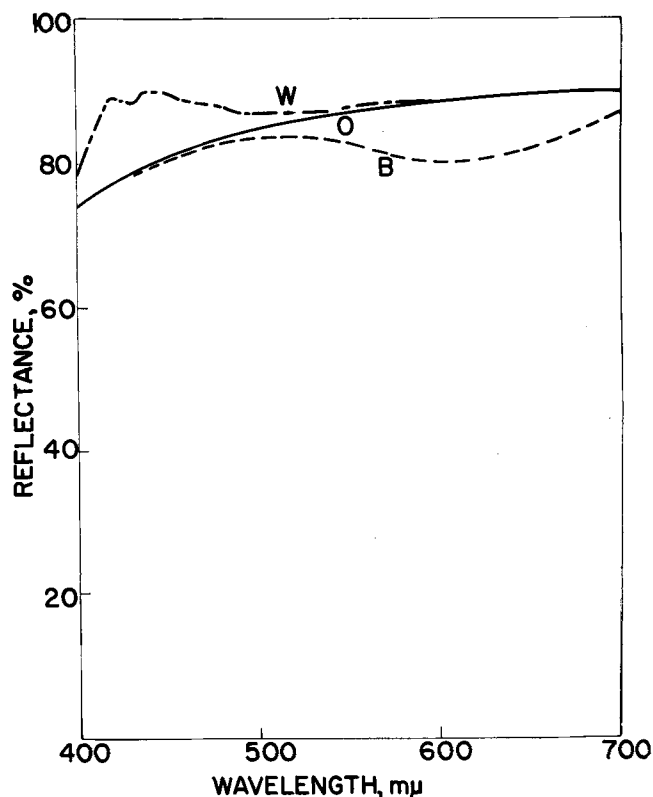
FIG. 3. Reflectance curves of bleached cotton cloth, before and after treatment with laundry blue and fluorescent whitener.

O —Original cotton cloth.
B —Same cloth treated with laundry blue.
W—Same cloth treated with fluorescent whitening agent (apparent reflectance curve).

acid sours. Other applications of brighteners are to textiles and paper in mill operations, in plastics, and in varnish and lacquer coatings. This discussion will cover mainly the application of brighteners in soaps and detergents. Some of the requirements of an optical bleach for use in soaps and detergents are as follows.

a) It must be free of any undesirable physiological properties.
b) It must be stable to soap and detergent processing and stable on storage in these products.
c) It must be substantive to textile fibers from a soap or detergent solution.
d) It must absorb ultraviolet energy but not absorb appreciable amounts of visible light.
e) It must have an intense shade of blue fluorescence, preferably close to 440 mμ.
f) It must meet certain fastness requirements.

A brightener's effectiveness in whitening a fiber depends upon how much of it leaves the wash solution and attaches itself to the fiber, its efficiency in converting ultraviolet light to visible light, and its shade of fluorescence. The working properties of brighteners in their application from soaps and detergents can be categorized in three main areas: build-up, fastness, and substantivity.

Build-up. This is a function of two factors, the concentration-fluorescence relationship and the percentage of exhaust. The concentration-fluorescence relationship is illustrated in Figure 5. Here the concentration of Brightener A[1] on cotton fabric is plotted *versus* its fluorescent intensity. At a concentration of 0.002% Brightener A produces more than

twice the fluorescent intensity as it does at one-half of this this concentration, 0.001%; however a concentration of 0.10% gives only about 8% more fluorescent intensity than one-half of this concentration, 0.05%. The concentration-fluorescence relationship varies with different brighteners; however none of the brighteners evaluated in this laboratory show a concentration-fluorescence curve of any greater slope than that of Brightener A.

The other factor in build-up is the degree of exhaustion of the brightener, *i.e.*, the ratio of the brightener affixing itself to the fiber to the brightener present in the wash solution at the beginning of the cycle. The percentage of exhaustion varies between about 40 and 95% with different types of brighteners. Factors that influence the exhaust are washing time, temperature, cloth-to-liquor ratio, type of detergent, builders, and pH. With heavy-duty detergents, where at least a ten-minute wash cycle and temperature of 120°F. are usually encountered, most of the cellulosic brighteners are nearly completely exhausted. Brighteners substantive to the noncellulosic fibers usually exhaust to a lesser degree. In nonionics or in soaps and anionic detergents without builders the rate of exhaust of most brighteners is quite often slower than in built anionic detergents, and therefore a greater percentage of the brightener will be left in the wash water at the end of the cycle.

In Figure 6 is shown build-up, the combination of concentration-fluorescence and exhaust factors. Sequential washes of three chemically different brighteners are plotted *versus* fluorescent intensity. The washings were carried out by using a typical anionic detergent. Concentrations of the various brighteners

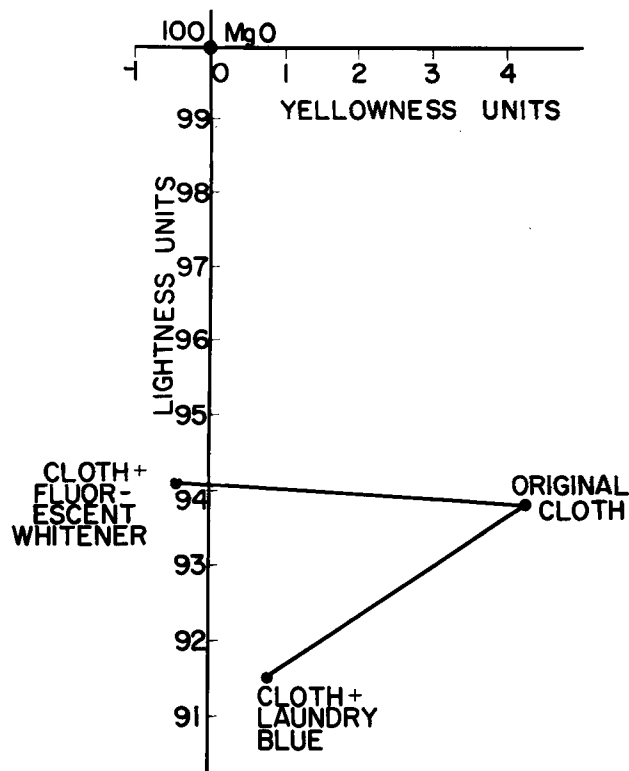[1] The structure of Brightener A and other brighteners to follow are shown in Figures 11 through 16.

FIG. 4. Yellowness and lightness values of cotton cloth, before and after treatment with laundry blue and fluorescent whitening agent.
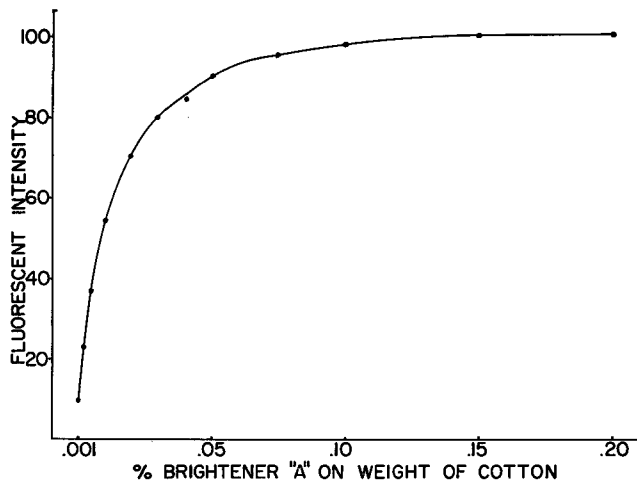
FIG. 5. Concentration-fluorescence relationship of triazinyl-stilbene brightener.
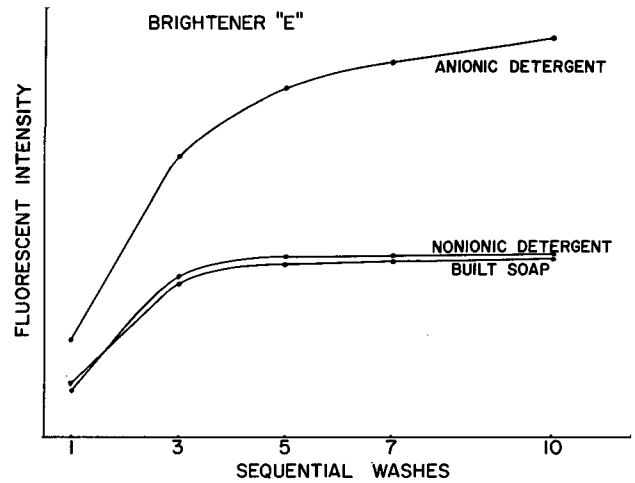
were adjusted to give equal whitening after one wash. Therefore it follows that the greatest potential whitening can be obtained with the brightener labeled A.

Fluorescence-sequential wash curves of Brightener E in different wash formulations, heavy-duty anionic and nonionic detergents, and a built soap are compared in Figure 7. It is evident that the washing formula has quite an effect on this brightener's per-
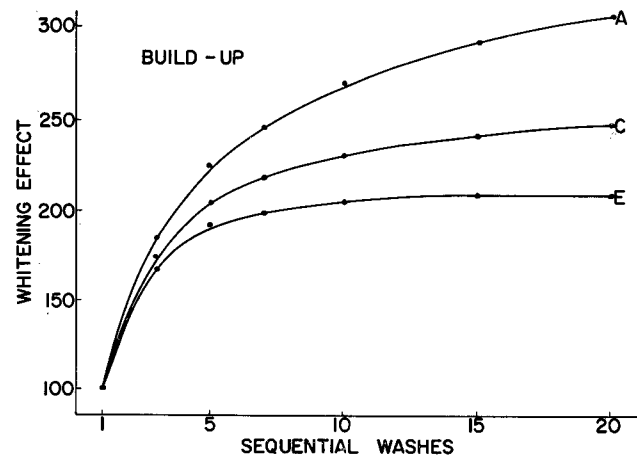

FIG. 6. A—Triazinylstilbene brightener; C—Benzidinesulfone brightener; E—Triazole brightener.

formance. There are other brighteners that behave in a similar manner while still others give essentially the same effect in all three washing media.

Fastness. By fastness is meant the retention of fluorescence. Fluorescence can be affected by bleaching compounds, sunlight exposure, alkali, and acid.

Bleach fastness of a brightener is an important consideration for its use in most detergents. All of the important commercially available brighteners for the soap and detergent trade are stable to perborate and other oxygen bleaches. They are also unaffected by reducing bleaches, such as sodium sulfite.

In the case of chlorine bleaches some brighteners are stable under all of the household methods of bleach application whereas others are stable only under certain bleach procedures. In general, once the brightener is attached to the fabric it is at most

FIG. 7. E—Triazole brightener.

only slightly affected by the bleach, *i.e.*, the brightener would be quite stable if the bleach were added in the wash water near the end of the cycle or in the rinse. However when the brightener itself is in contact with the bleach solution, it is a different matter. There are only a few brighteners that are unaffected under these conditions. The loss of brightening effect depends upon how long the bleach is present in the wash solution before the fabric is entered. In Figure 8 is shown the loss of fluorescence of a so-called non-hypochlorite fast brightener with the addition of bleach at various times in the washing cycle.

It is seen that if the fabric is entered before the bleach, there is little loss of fluorescence. Realizing that the bleach has little effect on the brightener once it becomes affixed to the fiber, it can readily be seen from the exhaust curve in Figure 9 why the loss of brightener effect is relatively slight when the fabric is present at the same time or before the bleach is added. In only 30 seconds the brightener exhausts to such an extent as to give nearly 80% of its optimum effect.
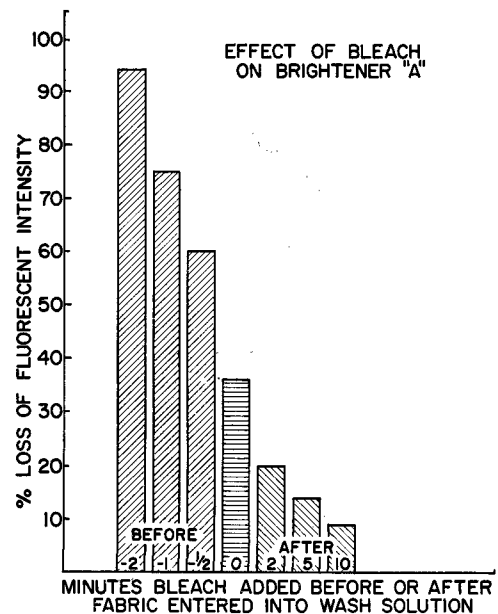

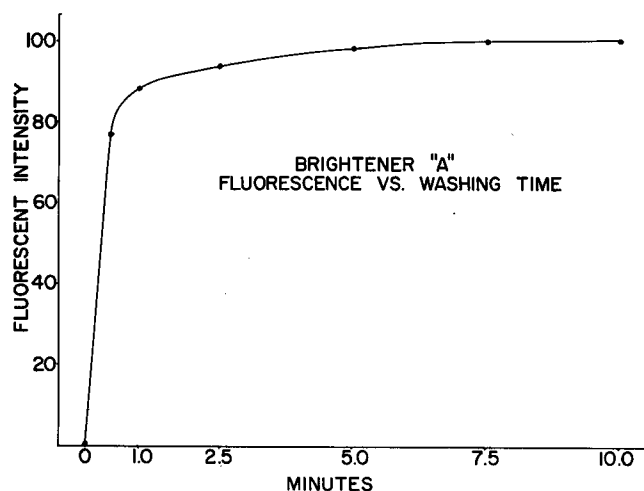FIG. 8. A—Triazinylstilbene brightener.

FIG. 9. A—Triazinylstilbene brightener.

The hypochlorite fastness of some brighteners varies with the washing formulation. In Figure 10 is shown the loss of fluorescence, because of the bleach, of two different brighteners, A and B, in heavy-duty anionic and nonionic detergents and a built soap (bleach added 30 seconds before cloth).

Another fastness property to consider is fastness to light. The optical bleaches used in soaps and detergents have relatively poor light fastness; however the light fastness of these products is quite sufficient for the end-use to which they are put, particu-
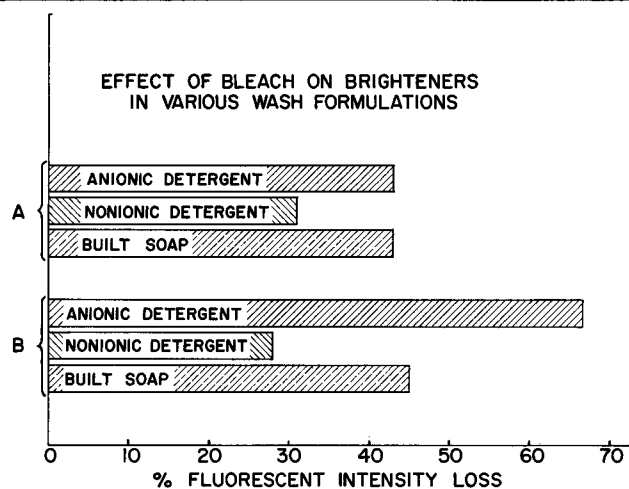

FIG. 10. Hypochlorite bleach added to wash bath 30 seconds before fabric entered.
    A—Triazinylstilbene brightener.
    B—Aroylstilbene brightener.

larly when it is considered that the fabric is replenished with brightener every time it is laundered. In most cases there is more brightener added in subsequent washings than is lost during exposure when the fabric is dried out of doors. Depending upon the type of brightener and the concentration applied, a fabric will lose from 15 to 50% of its fluorescence on exposure for five hours to direct sunlight on a midsummer day. The relatively poor light fastness can be attributed to both the nature of the brightener and to the low concentration on the fabric. In a single washing application only about 0.005% brightener is

applied to the fabric whereas with colored dyes the concentration could easily be more than 100 times as great.

The loss of fluorescence in a Fade-Ometer is much greater than in daylight. The brightener fades almost 10 times more rapidly than in daylight; therefore such an instrument should not be used for measuring directly the light fastness of brighteners. It can be used however in comparing their relative light fastness.

Some optical bleaches, based on the stilbene nucleus, such as Brightener A in Figure 11, when in solution are not stable to light of short wavelength radiation. These brighteners are converted from the *trans* to the ineffective *cis* isomer. This instability is of little consequence in actual use but does present a problem in testing. If a brightener stock solution is allowed to stand in a clear glass container exposed to daylight, fluorescent, or incandescent light, it will gradually lose strength. Our brightener application laboratory at American Cyanamid is illuminated with yellow mosquito-repellent lamps. Long wavelength light, such as this, does not adversely affect the brightener. Daylight illumination would be satisfactory if the brightener solution were stored in low actinic glassware.

For an optical bleach to be of much value for soap and detergent use, it should be stable to an alkaline pH of at least 10. Most of the brighteners are stable to a pH of at least 12; however there are a few that decompose on storage at high pH or at high pH together with high temperature, as would be the case in the spray drying of a detergent.

Most of the brighteners are not adversely affected by mild acid after-treatment of the fabric. There are one or two commercial brighteners that are acid-sensitive. These will turn yellow if the brightener-dyed fabric is subjected to an acid sour or sometimes even to acid perspiration.

Although most of the brighteners once affixed to the fiber are not adversely affected by acid, relatively few can be applied to cotton at a low pH. These products that are effective at low pH often find use in acid sour formulations in the commercial laundry trade.

Substantivity. Up to this point the application of optical bleaches primarily to cellulosic fibers has been considered. Although cotton does represent about 80% of the housewife's washing and even a greater percentage of that of the commercial laundry, synthetic fabrics are becoming increasingly important. Also there is more and more resin-treated cotton which does not accept brighteners to the same degree as untreated cotton. Today's commercially available brighteners can be classified, as to their substantivity for various fibers, into three major groups: those substantive to only cellulosic fibers, such as cotton and viscose rayon (I); those substantive to nylon as well as to cellulosics (II); and those substantive to only noncellulosics, such as nylon, acetate, wool, silk, and Arnel, cellulose triacetate (III).

Until a few years ago only cellulosic specific brighteners were incorporated in the big-volume soap and detergent products; however recent developments in the dye industry made available brighteners substantive to nylon as well as cotton. Although these brighteners do impart a considerable whitening effect to nylon, they are more substantive to cotton. In a typical heavy-duty anionic detergent these so-called

all-purpose brighteners produce about twice as much whitening of cotton as nylon, such as the duPont type 200 nylon. With a more opaque and less dyeable nylon, such as type 670, the whitening effect is only about one-quarter as great as on cotton. In the case of some all-purpose brighteners the effect on nylon is reduced even farther when cotton is present with the nylon in the wash load. The brightener, having more affinity for the cotton, is preferentially absorbed. Some all-purpose brighteners do not exhibit this preferential behavior. They give essentially the same effect in a mixed load as in an all-nylon wash.

It is sometimes advantageous to use a combination of a cellulosic specific and a noncellulosic brightener in a wash product. Not only is cotton and nylon whitened but also other fibers such as acetate, Arnel, wool, and silk. Cotton does not compete with the noncellulosic fibers for brightener since each brightener is specific for one class of fibers.

All of the cellulosic and all-purpose brighteners show a decreased substantivity for resin-treated cotton. The whitening effect of resin-treated cotton, in general, is about 25 to 70% as great as that of cotton without resin. Usually those brighteners that are substantive to nylon as well as cotton give the greatest relative effect. An exception is the amino coumarin type of brightener which is normally substantive to noncellulosic fibers such as nylon, acetate, and wool but not to cotton. It has slight substantivity for resin-treated cotton.

There are today six major chemical classes of brighteners used in the soap and detergent trade. In Figures 11 through 16 are structures representing these classes. These are Brighteners A, B, and C (Group I), D and E (Group II), and F (Group III).
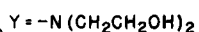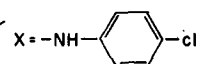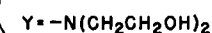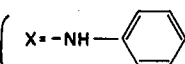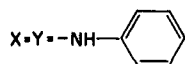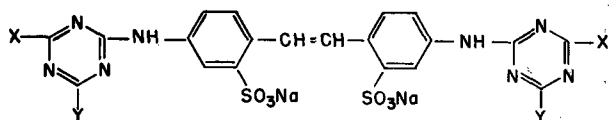

FIG. 11. Triazinylstilbenes.

Brightener A, of the tranzinyl diaminostilbene class shown in Figure 11, is often referred to as the work-horse brightener since it is exceptionally efficient in whitening cotton and is used extensively. It has excellent build-up properties. It gives equally good results in anionic and nonionic detergents and built soaps. It exhausts rapidly and nearly completely. Once on the fiber, it has good hypochlorite fastness but is not very stable to hypochlorite in solution. It is usually incorporated in detergents together with a brightener that has good hypochlorite fastness. Under optimum conditions it whitens the soap or detergent in which
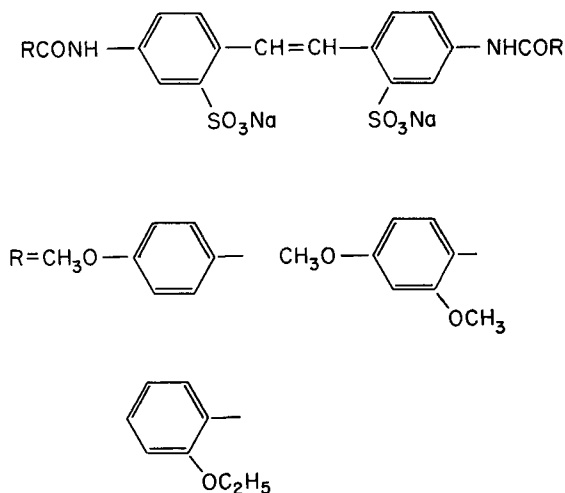

FIG. 12. Aroylstilbenes.

it is incorporated. It is not as effective at a low pH as at a neutral or alkaline pH.

Brightener B, of the aroyl diaminostilbene class shown in Figure 12, is not as effective as Brightener A in alkaline-washing formulations. It imparts a yellow tint to the product in which it is incorporated. Its greatest utility is in low pH applications, such as in acid sours for use in the commercial laundry trade.
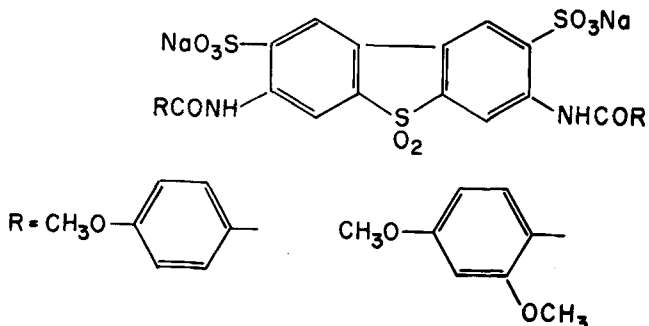

FIG. 13. Benzidinesulfones.

Brightener C, of the aroyl benzidinesulfone class shown in Figure 13, is not as efficient as Brightener A in whitening cotton but does find extensive use because it has excellent hypochlorite stability. It can be incorporated directly in chlorine bleach products. It is effective at both acid and alkaline pH and is equally as effective from nonionics as anionic detergents.

Brightener D, of the bisbenzimidazole class shown in Figure 14, is quite often referred to as an all-purpose brightener. By all-purpose is meant good hypochlorite fastnesss and substantivity to nylon as well as cotton. This brightener also has slight substantivity for acetate. Although it does have good
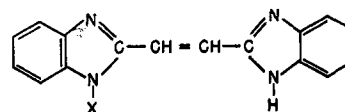

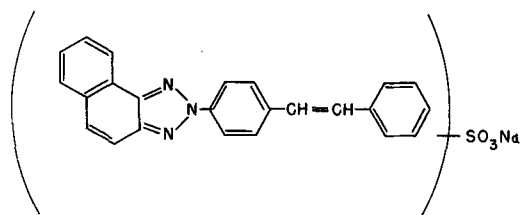X = H OR ALKYL

FIG. 14. Bisbenzimidazoles.

FIG. 15. Triazole.

hypochlorite fastness in a normal home-laundry application, it does not have the stability required for incorporation into a chlorine bleach product. It is equally as effective in anionic and nonionic detergents and built soaps. An outstanding feature of Brightener D is its good compatibility with cationic agents.

Brightener E, of the triazole class shown in Figure 15, in most respects is like Brightener D. Unlike the latter it is not as effective from nonionic detergents and soaps as from anionic detergents. It is not acid-sensitive and can be applied to cotton at a low pH. It lacks compatibility with cationics, as do most of the brighteners that are substantive to cellulosics.
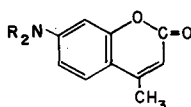

R = ALKYL

FIG. 16. Amino coumarins.

Brightener F, of the amino coumarin class shown in Figure 16, is a whitener for fine fabrics. It has poor hypochlorite stability in solution but good fastness when once affixed to the fabric. Since it is used mainly in light-duty detergents recommended for fine fabric laundering, its poor hypochlorite stability is usually not a drawback. This type of brightener is often incorporated in perborate bleach products. Although it is not substantive to cotton from soap or detergent solutions, in conjunction with cationic agents, such as fabric softeners, it does dye cotton.

MODIFIED GM FLUORIMETER

A= F4P5 UV SOURCE

B= FILTER ISOLATES 300-400 mu
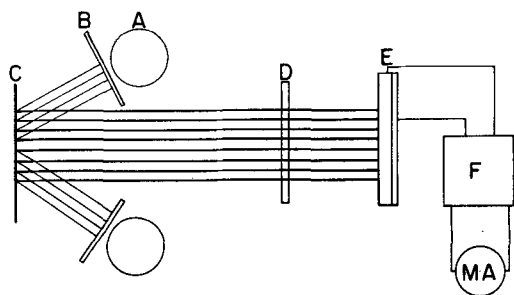
C= SAMPLE

D= FILTER ISOLATES 400-500 mu

E= PHOTOMULTIPLIER

F= VACUUM TUBE VOLTMETER

FIG. 17. Instrument for measuring brightener treated fabric.

Evaluation

There are three major methods of evaluating brightener-treated fabric. These are by instrument (such as a Modified G. M. Fluorimeter), visual examination under an ultraviolet lamp, and visual examination in daylight.

Measurement of Fluorescence with Fluorimeter. The fluorimeter provides the most precise method of determining fluorescence. A strength difference of 1.5% can be detected easily. In Figure 17 is illustrated a diagram of the Modified G. M. Fluorimeter. Radiation from a black light ultraviolet lamp A (F4P5) passes through a filter B (Corning No. 5860 Violet Ultra Filter Glass), which cuts out all visible light. The ultraviolet radiation then strikes the sample and is partially converted into visible blue light. This blue fluorescence then passes through filter D (Wratten No. 47A), which screens out any reflected ultraviolet radiation. The visible blue light then impinges on a photomultiplier tube E (931-A) where it is converted to electrical energy and is amplified. Readings are made on a vacuum tube voltmeter against a suitable standard. The readings thus obtained do not indicate the efficiency of the measured fluorescence, nor do they describe the shade of fluorescence. These readings however do have meaning when the fluorimeter is used to measure the fluorescence of one brightener under various application conditions, such as the loss of fluorescence because of hypochlorite treatment, the increase in fluorescence with an increase of brightener concentration, the increase upon sequential washes, etc. It can be used for comparing chemically similar brighteners or even chemically different brighteners, providing their absorbing and emitting characteristics are the same, *i.e.*, if they absorb the same wavelength light and produce the same wavelength of emission.

Although optically different brighteners cannot be measured directly on the fluorimeter for whitening efficiency, they can be compared by using a correction factor. The factor corrects for the discrepancy between the energy distribution of the fluorimeter's ultraviolet light source and that in daylight and the discrepancy between the response curve of the photomultiplier tube plus filter and the theoretically desired response. Also the factor converts fluorescence intensity to effective fluorescence intensity, *i.e.*, whitening and brightening efficiency. Specialized equipment is required for obtaining data for calculating the correction factor. Eugene Allen of the Research Division of the American Cyanamid Company has done considerable work in this field (8).

Figures 18–21 indicate why a correction factor is required. In Figure 18 are shown the ultraviolet absorption curves of five different optical bleaches. The location of the absorption peaks varies. Keeping these variations in mind and observing the energy distribution curves of the fluorimeter's ultraviolet light source and sunlight shown in Fighre 19, it can be seen that those brighteners which absorb most strongly at about 350 mμ will be favored in the fluorimeter (curve B) whereas those that absorb between 390 and 400 mμ actually show to best advantage in daylight (curve C).

In Figure 20 the emission curves of the same five brighteners are shown. The peaks vary from 435 to 455 mμ. The fluorimeter is more sensitive to the shorter wavelength fluorescence whereas the eye is
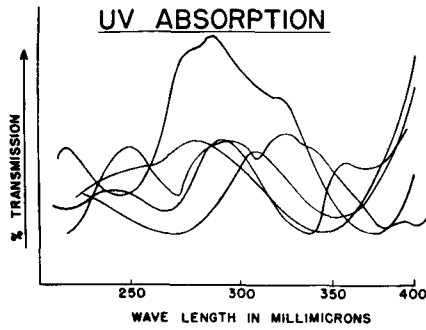
UV ABSORPTION

FIG. 18. Five chemically different optical bleaches.

more sensitive to the longer wavelengths (Figure 21). Thus this is another discrepancy that requires correction. Even if the instrument were such as to have a light source equivalent to daylight and it were modified to read all of the fluorescence emitted and it were corrected for the eye sensitivity, there would remain still one uncorrected factor. It would still be necessary to weight the fluorescent intensity as to efficiency in compensating for yellowness and brightening the fabric. If, for example, a structure fluoresced strongly in the green region of the spectrum, it would not whiten the fabric but would nevertheless register a high reading.

Visual Examination Under Ultraviolet Lamp. A second method of evaluation is one in which the fluorescence of brightener dyeings is compared visually under an ultraviolet lamp. In comparing similar shade brighteners, strength differences of 5% can readily be seen. Strengths of optically different brighteners obtained in this manner do not necessarily indi-
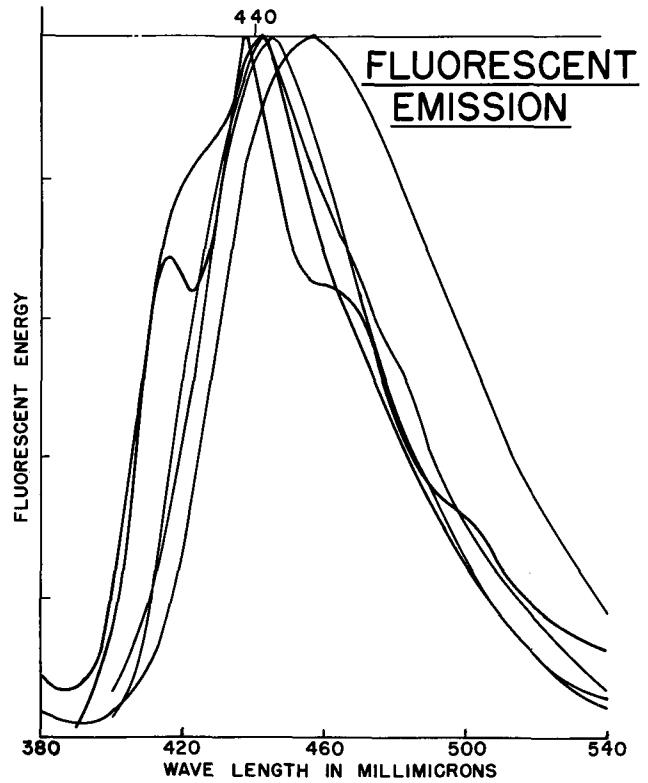
FLUORESCENT EMISSION

FIG. 20. The same five chemically different optical bleaches as in Figure 18.

cate daylight whitening power for very much the same reasons that were pointed out for fluorimeter readings. However it does afford a quick method of determining strengths of brighteners with similar optical properties and the same brightener before and after subjection to certain fastness tests or under different application conditions. Also, by visual examination under ultraviolet light, it is easy to determine the shade of a brightener. If the brighteners that are being compared absorb ultraviolet light in essentially the same region, it is possible with practice to predict from their shade and intensity of fluorescence about how they will compare in daylight.

A phenomenon that one should be aware of when viewing brightener dyeings under ultraviolet light is the "Schonfelder effect." This is the fact that the eye is more able to detect small differences in shade after it has become adapted to that kind of light being viewed. In practice this means that smaller shade differences can be detected five to ten minutes after working with the samples under ultraviolet light than when they are first examined. Another important effect, the "Bezold Brucke effect," is that the apparent hue of some colors change with the intensity of light. In practice this means that a brightener will appear redder when held farther from the light source. The same effect occurs if the concentration of brightener on the fabric is reduced. It is important therefore when comparing brighteners for shade that the intensity of fluorescence of the samples being compared be equal.

Visual Examination in Daylight. By examining an optical bleach in daylight, it is possible to get essentially the same impression of whiteness that the housewife receives when she looks at her wash hanging on the line—essentially the same impression because day-
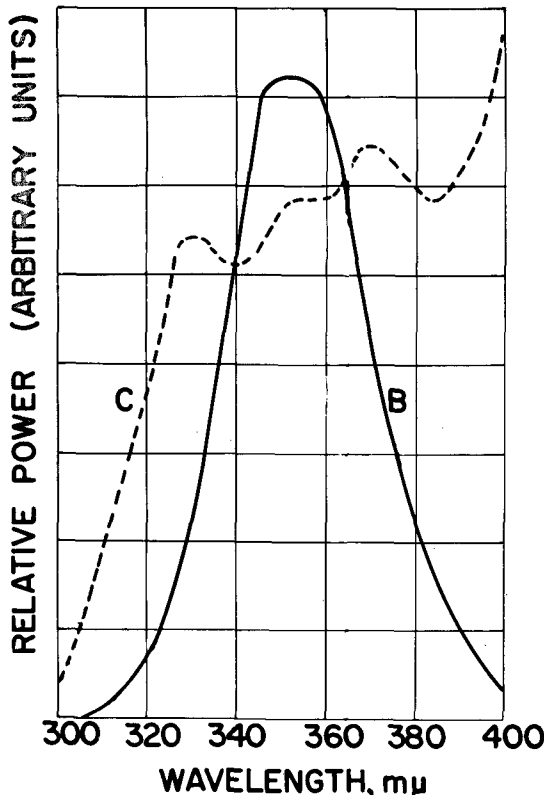
FIG. 19. Distribution of energy from different light sources.
B—T12 black light lamp with integral filter
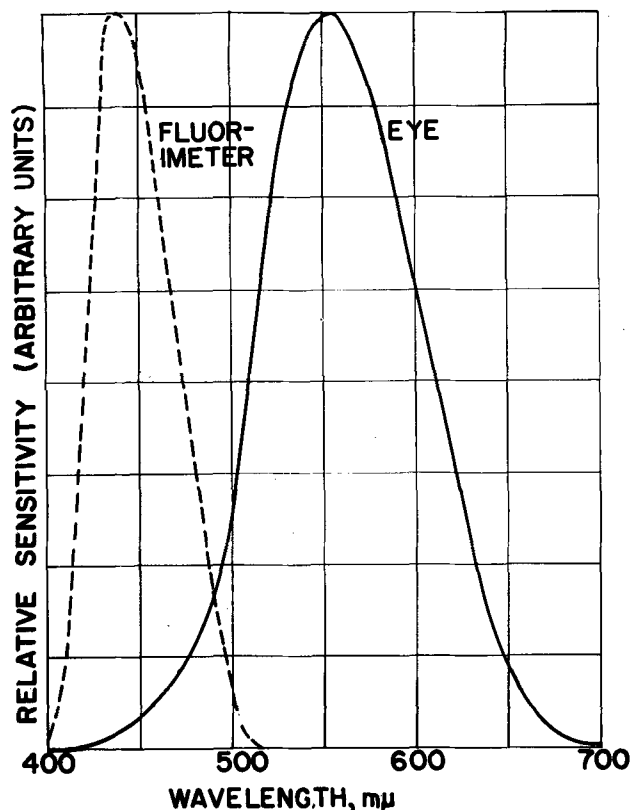C—Daylight (Middleton)

FIG. 21. Relative sensitivity of human eye and of fluorimeter to different wavelengths of light.

light varies in spectral quality from day to day or even from minute to minute. To obtain consistent results an artificial light source that approximates daylight can be used. Such a light source in Macbeth's C-4D Examolite Model UV. It is also considered desirable to evaluate brighteners under fluorescent and incandescent light since the housewife also examines her laundry under such lighting.

There is one main disadvantage in evaluating brighteners visually in daylight or artificial white light, and, that is, it is not very precise. Ten per cent differences in strength of a brightener are barely apparent. With different shade brighteners, personal shade preference influences the evaluation. Therefore the evaluation is not strictly one of whitening effect but rather whitening effect and shade preference. For such ratings to be significant a fairly large panel of observers is required. It should be pointed out that when brightener dyeings which differ considerably in shade are compared side by side, the difference is accentuated. For example, when a red shade brightener (one whose emission peak is about 435 mμ) is compared to a green shade brightener (one whose emission peak is about 455 mμ), the former will appear redder and the latter greener than would be the case if each were observed by itself. It therefore is sometimes advantageous to compare samples indirectly, i.e., place an untreated piece of fabric between the brightener dyeings and compare each to the untreated cloth.

To obtain reproducible evaluation data, visual or instrumental, the brightener-treated fabric should always contain the same amount of moisture. At the American Cyanamid Company the dyeings are conditioned for four hours at 65% R.H. and 70°F. before making evaluations. In Table I can be seen the

TABLE I

Cotton Fabric Containing 6.5% Moisture Used as Standard
Effect of Moisture on Fluorescence of Cotton

Brightener	6.5% Moisture	0% Moisture	65% Moisture
A	100	76	96
A-1	100	88	85
C	100	100	98
D	100	92	100
E	100	98	97

differences in fluorescent intensity of various brighteners with different amounts of moisture present in the fabric. Six and one-half per cent moisture is present in 80 x 80 motton conditioned at 65 R.H. and 70°F. A percentage of nearly zero is encountered immediately after ironing of the fabric and 65% upon putting the wet fabric through a wringer. It may be well to evaluate a brightener under these latter conditions to determine how it will appear to the housewife when she is doing her ironing or hanging her wash out to dry.

Summary

In this discussion a brief history of optical bleaches and some chemical aspects of brightener structures have been presented. A description has been given of the behavior of optical bleaches in soaps and detergents and of several methods by which they are evaluated. It has been attempted to show the various choices a soap or detergent manufacturer has with the current commercially available brighteners. The differences between these brighteners as to substantivity, degree of exhaustion, fastness properties, etc., have been pointed out. Also it has been shown that certain brighteners differ in behavior with variations in the detergent formulation and washing procedure.

Acknowledgment

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