Optical Bleaches on Wash-and-Wear Cotton

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THE TREMENDOUS growth in popularity of wash-and-wear fabrics in recent years has created a challenge for those of us interested in optical bleaches. We are faced today with the necessity for providing an optical bleach which is as effective for wash-and-wear fabrics as those we now have for untreated cotton. Before discussing the problems inherent in the wash-and-wear situation, it would be well to examine briefly the optical aspects of these comparatively new bleaching agents.

Optical Effect

Optical bleaches, which are also referred to as brighteners, whitening agents, and fluorescent bleaches, can be classified as dyes. A nonfluorescent dyed substance, placed in daylight or artificial white light, reflects part of the light striking it and absorbs 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.

Color is usually thought of by the layman 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 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 is probably the easiest way of understanding the principles that underlie this new bleaching method.

Figure 1 shows reflectance curves of bleached 80 × 80 cotton fabric and of magnesium oxide, which is commonly accepted as the standard for whiteness (1). Curve O 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, or conversely more yellow light is reflected and the fabric therefore appears yellow. Thus the fact that the curve is lower and slopes down 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.

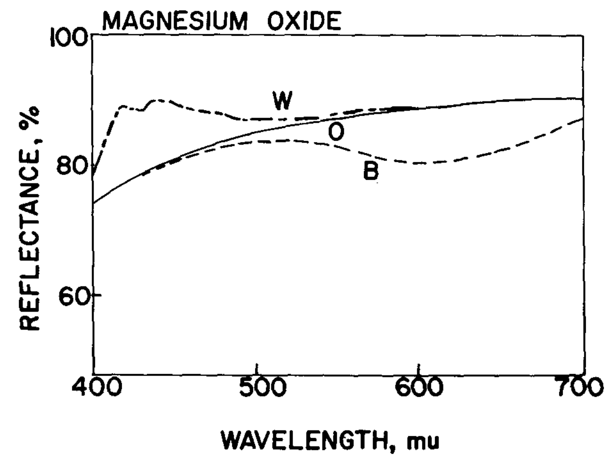

FIG. 1. Reflectance curves of bleached cotton cloth, before and after treatment with laundry blue and fluorescent whitener.
O — Original cotton cloth.
B — Same cloth treated with laundry blue.
W — Same cloth treated with fluorescent whitening agent (apparent reflectance curve).

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 ultraviolet energy which is present in daylight, fluorescent, and incandescent light. It converts the otherwise unused invisible ultraviolet energy to visible blue light. Curve W 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 lighter.

Brightener Development

It was about 10 years ago that optical bleaches began to be used extensively, first in soaps and detergents and later in mill applications to textiles and paper. The earlier brighteners incorporated in soaps and detergents were substantive to only cellulosic fabrics and lacked hypochlorite bleach stability. In 1950 American Cyanamid developed a hypochlorite fast cellulosic brightener, which found extensive use in detergents and dry chlorine bleaches. A few years later specialty product manufacturers began to use a fine fabric brightener, one substantive to wool, silk, nylon, and acetate. Approximately five years ago the all-purpose optical bleaches started to find extensive use. These all-purpose types are not only substantive to cotton and viscose but also to nylon and possess a fairly high degree of chlorine bleach stability.

Today many of the dyestuff manufacturers are putting emphasis on the development of optical bleaches that are more effective in whitening wash-and-wear fabrics than are the currently available brighteners.

Importance of Wash-and-Wear

What is a wash-and-wear or, more appropriately, a minimum-care, fabric? It is one that requires little ironing after laundering and resists wrinkling during wear. Little more than a novelty five years ago, wash-and-wear is now a major factor in the market.

In 1958 wash-and-wear production of shirts was 189 million units, about 50% of total production. Slightly more than 90% of the wash-and-wear was resin-finished cotton whereas less than 10% was represented by synthetics or synthetic blends, such as polyester fibers and polyester fiber blends (2).

A substantial share of cotton production is going into wash-and-wear. In Table I is shown the percentage of men's and boys' apparel that was resin-finished last year (2). It is seen that work shirts represented only a very minor share of wash-and-wear production. Since most work shirts are colored, they should not be given much consideration as far as brighteners are concerned.

TABLE I

Men's and boys' apparel	Resin finished share of total cotton production
Shirts	
(Dress)	60%
(Sport)	65
(Work)	3
Trousers	
(Dress and sport)	59
(Work)	10
Outer Jackets	34
Sport Coats	25
Bathrobes	30
Pajamas (woven)	40
Under shorts	15

The percentage of domestic cotton items that are resin-treated, as shown in Table II, is somewhat less than that of men's and boys' wearing apparel (2). However I think we shall see an increase in the future in the production of wash-and-wear domestic items, especially sheets and pillow cases.

TABLE II

Domestic items	Resin finished share of total cotton production
Bedspreads (woven)	15%
Curtains (excl. lace and shower)	30
Sheets	10
Pillow cases	8
Table cloths	5
Retail piece goods	40

Wash-and-wear is continually expanding. One of the nation's largest shirt manufacturers states that 60% of its 1958 dress shirt production was wash-and-wear, 70% of 1959 production was wash-and-wear, and 80% of 1960 production is expected to be wash-and-wear.

Mechanism and Chemistry of Wash-and-Wear Finishes

Cellulose is generally considered to be predominantly composed of anhydroglucose units linked together through an ether group. Cellulosic fibers are composed of bundles of cellulose chains made up of these anhydroglucose units. When a cellulosic fiber is wrinkled, it is believed that these cellulose chains slip past each other into new equilibrium positions.

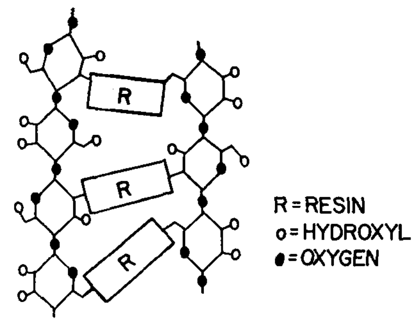

FIG. 2. Resin molecules crosslinking two adjacent cellulose chains.

Recent work shows that the resins used for imparting wrinkle recovery chemically react with these cellulose chains. It is believed that cross-links are formed between adjacent cellulose chains or microfibrils within the fiber (3, 4, 5).

Figure 2 schematically shows resin molecules crosslinking two adjacent cellulose chains. This crosslinking would tend to prevent the cellulose chains slipping past one another under applied stress. It is believed that this cross-linking increases the elasticity of the fiber and therefore its ability to recover from deformation, which in turn is responsible for its wrinkle-recovery and wash-and-wear properties.

Although the chemicals used to impart wrinkle recovery are called resins, they actually are mostly in monomeric form when applied to textiles (6). Therefore they are small enough to diffuse inside a water swollen fiber and chemically to react with and crosslink the adjacent cellulose chains.

The textile chemicals commonly used for imparting wrinkle recovery are based on reaction products

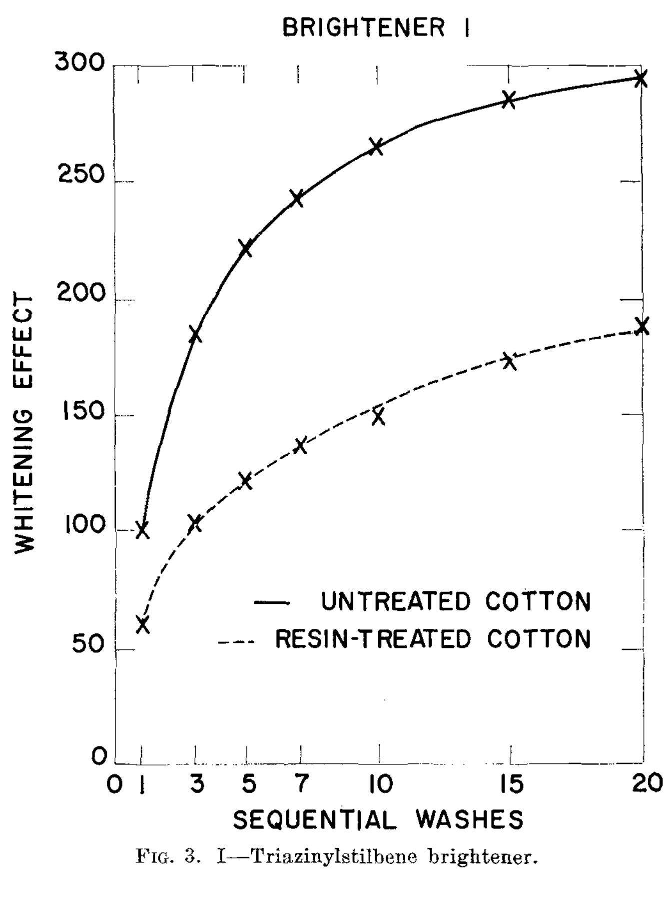

FIG. 3. I—Triazinylstilbene brightener.

of formaldehyde with urea, ethylene urea, triazone, and triazine. Two relatively new finishes are the epoxy resins and the Belfast finish. Neither type contains nitrogen and is not based on formaldehyde.

Brightener Application

How does wash-and-wear cotton differ from untreated cotton in its behavior with the brighteners contained in today's detergents?

In Figures 3 through 7 are sequential wash-curves of the five brighteners most commonly incorporated in the current detergents. The whitening effect of triazone resin-treated cotton is compared with that of untreated cotton upon laundering in a typical heavy-duty anionic detergent containing brightener. The triazone resin is one of the commonly used wash-and-wear finishes. The treated and untreated fabrics were washed in separate baths.

Brightener I, a triazinyl stilbene type, probably the largest volume brightener incorporated in detergents today, is shown in Figure 3. It is aptly referred to as the workhorse brightener. As well as being very effective in whitening cotton, it has slight substantivity for nylon.

It is seen that after one wash the brightener is only 60% as effective on resin-treated cotton as on untreated cotton. A difference of 3% in whitening effect is discernible by the naked eye. Twenty sequential washes of this brightener on resin-treated cotton produces a whitening effect about equivalent to three applications on untreated cotton.

Another triazinyl stilbene, Brightener II (Figure 4), gives an even poorer relative effect than Brightener I. Like the former, it builds up exceptionally well on untreated cotton; however, unlike Brightener I, it has practically no affinity for nylon. Twenty sequential washes with Brightener II produce less whitening of resin-treated cotton than two washes on untreated cotton.

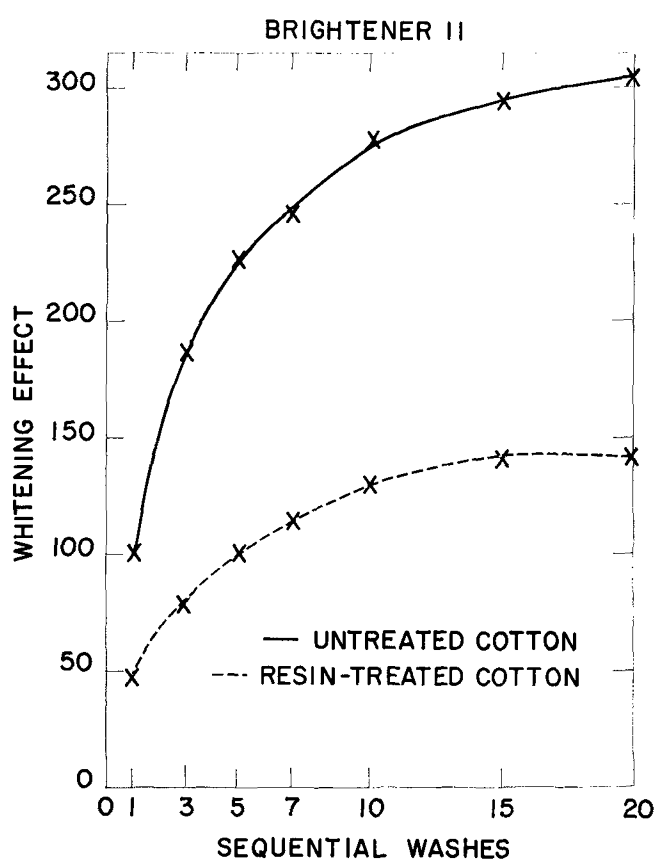

FIG. 4. II—Triazinylstilbene brightener.

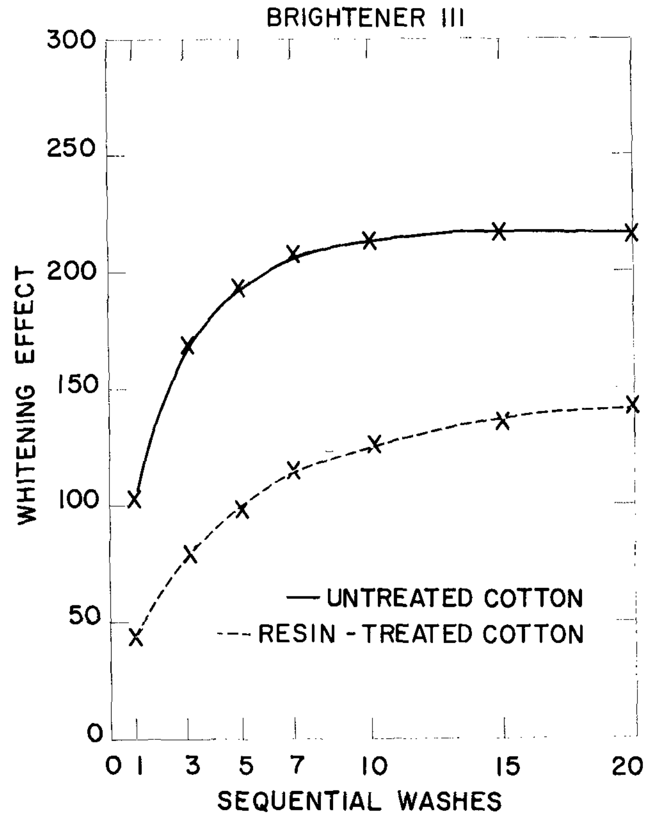

FIG. 5. III—Benzidenesulfone brightener.

The benzidine sulfone, Brightener III, which has excellent hypochlorite stability and is substantive to only cellulosics, is compared in Figure 5. It, too, is much less effective on resin-treated cotton than on untreated cotton.

The all-purpose type, Brightener IV, which is a naphthotriazole, is compared in Figure 6. This brightener has relatively good hypochlorite fastness and is subtantive to nylon as well as to cellulosics. It is about 74% as effective on resin-treated cotton as untreated after one wash. After twenty sequential washes its resin-treated cotton whitening is almost equivalent to untreated cotton whitening. This relatively good build-up may be a little misleading because Brightener IV does not have a particularly good build-up on untreated cotton. Actually Brightener I (Figure 3), which is far inferior on resin-treated cotton to untreated cotton after 20 washes, is actually slightly superior in build-up on resin-treated cotton to Brightener IV.

Another all-purpose type, Brightener V, a benzimidazole which more nearly approaches the ideal than any of the other brighteners as far as wash-and-wear whitening is concerned, is shown in Figure 7. Like Brightener IV, it has relatively good hypochlorite fastness and is substantive to nylon as well as to cellulosics. Its effect on resin-treated cotton *versus* untreated is 76% after one wash and more than 80% after 10 and 20 sequential washes. This effect on resin-

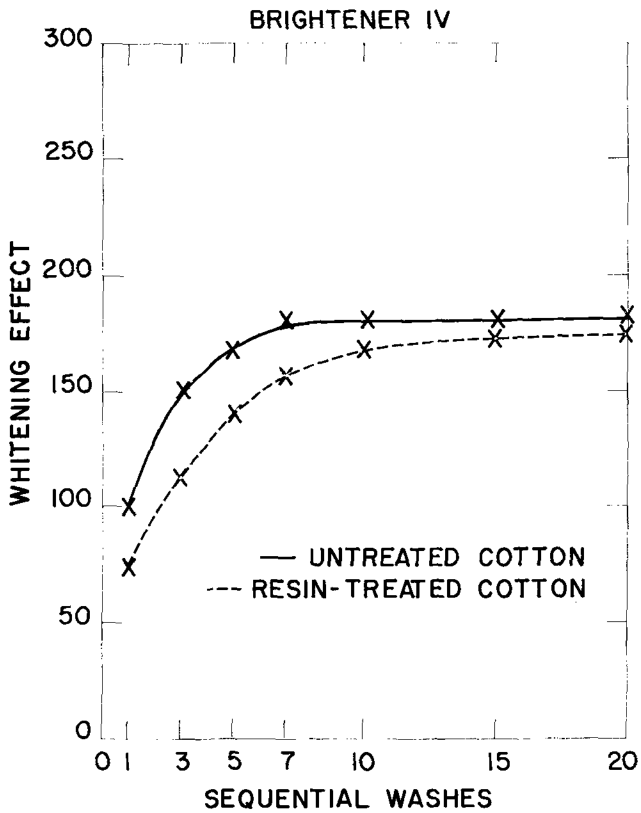

FIG. 6. IV—Naphthotriazole brightener.

treated cotton is appreciable, considering the fact that it is being compared with its exceptionally good build-up on untreated cotton. Brightener V differs from the previous four brighteners in that it is nonionic.

Brighteners I–IV are anionic, and all contain two sulfonic acid substituents except IV, which has one sulfonic acid group. Brightener V has one major undesirable feature, acid sensitivity. Acid sours, acid fumes, and acid perspiration will cause it to yellow. Thus it would appear that the ideal brightener is not yet available for this particular resin finish or for other resins, as will be shown by subsequent data.

In Table III are comparisons of these brighteners on various fabrics. Also included is a fine fabric brightener (VI), an amino coumarin type substantive primarily to nylon, wool, silk, and acetate. Data for the ethylene urea finish are not noted. Actually the whitening effect obtained on this fabric falls between that of the other two nitrogen-containing resins, the triazone and triazine. These comparisons are on the basis of one wash, using a heavy duty anionic detergent. Except for Brightener VI, the concentrations of brighteners used were such as to give equal whitening effect with one another on untreated cotton. This effect was then arbitrarily rated 100. With Brightener VI, the effect on nylon (Type 670) was used as standard and rated 100. With all the cellulosic brighteners the effect on the Belfast-treated cotton most nearly approaches that on untreated cotton. Of course, this effect is reduced when Belfast is topped with other resins. This is often done in order to supplement its wash-and-wear properties. An interesting correlation is the effect obtained with the nitrogen type of resins and the polyamide fiber, nylon. The brighteners that are most effective on nylon are also most effective on triazone and triazine resin-treated cotton. The triazinyl stilbene, Brightener II, and the benzidine sulfone, Brightener III, which have practically no affinity for nylon, are rated lowest. It is interesting to note also that the amino coumarin, Brightener VI, which is much more effective on nylon than cotton, is stronger on resin-treated cotton than on untreated cotton.

TABLE III

Relative Whitening Effect

Brightener	I	II	III	IV	V	VI
Untreated cotton	100	100	100	100	100	13
Triazone	59	49	42	74	76	27
Triazine	39	19	16	43	60	64
Epoxy	74	51	69	64	70	40
Belfast	94	90	91	95	93	29
Untreated nylon	10	2	3	35	32	100

I—Triazinylstilbene, II—Triazinylstilbene, III—Benzidenesulfone, IV—Naphthotriazole, V—Bisbenzimidazole, VI—Aminocoumarin.

All of the data presented up to this point are based on separate launderings of the various fabrics. What also should be considered are the effects obtained with mixed wash loads. In Table IV is shown relative whiteening effects of Brighteners I–V on an all-untreated cotton wash load, on all triazone, and on triazone in a 50–50 wash load of triazone-finished cotton and untreated cotton. These brighteners, having more affinity for cotton, are preferentially absorbed on the untreated material; therefore this results in a reduced effect on the resin-treated cotton. The presence of untreated cotton would make little difference in the effect on the resin-treated cotton in the case of the fine fabric brightener (VI), which has only slight affinity for untreated cotton.

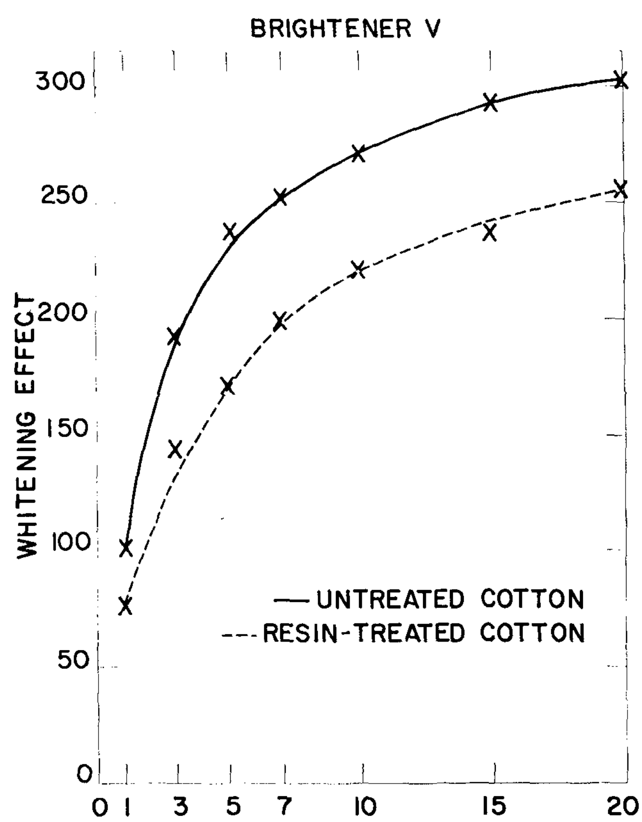

FIG. 7. V—Bisbenzimidazole brightener.

TABLE IV
Relative Whitening Effect

Brightener	I	II	III	IV	V
Untreated cotton	100	100	100	100	100
Triazone	59	49	42	74	76
Triazone (½ of load untreated cotton	38	27	25	56	58

I—Triazinylstilbene, II—Triazinylstilbene, III—Benzidenesulfone, IV—Naphthotriazole, V—Bisbenzimidazole.

The main reason why brighteners give weaker results on wash-and-wear cotton is that they have less affinity for this chemically modified fiber. With a brightener, such as the triazinyl stilbene type (I), about 25% of the initial brightener remains in the detergent bath after the washing cycle, and approximately 25% is removed from the triazone resin-treated fabric in the rinse cycle. Upon sequential washing, the amount left behind becomes progressively greater. What also contributes to the reduced effect is the fact that most wash-and-wear cotton absorbs more UV radiation than does untreated cotton. In addition, wash-and-wear contains less moisture. At 65% R. H. and 70°F. resin-treated cotton contains about 25% less moisture than untreated cotton. Most brighteners fluoresce less strongly as the moisture content of the fabric is reduced.

We have seen that with most of the wash-and-wear finished cotton the current optical bleaches give a substantially reduced initial effect. This effect is reduced even further when the fabric is exposed to sunlight. The loss of fluorescent intensity of most brightener-treated resin-finished cottons is 25% to 30% greater than brightener-treated cotton without the wash-and-wear finish. Another fastness property to consider is hypochlorite fastness. Those brighteners which have good hypochlorite fastness on untreated cotton still have good hypochlorite fastness on resin-treated cotton. Those brighteners that are poor in hypochlorite fastness on untreated cotton are poorer still on resin-treated cotton, especially when bleach is added early in the washing cycle. The reason for this reduced effect is that the brightener exhausts more slowly onto wash-and-wear cotton, therefore there is more time for it to be attacked by bleach before it attaches itself to the fiber. Once on the fiber, the brightener has reasonably good fastness to bleach.

All of the resin-treated fabrics used in gathering these data were prepared under controlled conditions in our Textile Chemicals Laboratory. The brightener effect on commercial wash-and-wear cotton could differ somewhat from our results. Factors that might cause differences are the amount of resin solids applied, type of catalyst used, curing time and temperature, and such additives as softeners, lubricants, and hand modifiers.

Summary

More than 50% of certain classes of wearing apparel, such as men's shirts, currently being sold are made of wash-and-wear fabric. This percentage is expected to increase even more in the future.

The reaction products used in preparing wash-and-wear cotton and the proposed mechanism whereby these products modify cotton have been described.

Data have been presented to show the reduced whitening effect and fastness properties obtained with the current optical bleaches on wash-and-wear cotton as compared with untreated cotton.

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A Report on the Problem of Residual Solvent in Solvent-Extracted Meals[1]

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SOLVENT-EXTRACTION METHODS are used for at least 90% of the soybeans and 30% of the cottonseed processed in the United States. Solvent processes are also used on flaxseed, safflower seed, rice bran, and others. Because the process yields quality products at a high extraction efficiency and can be operated continuously and economically in medium-to-large installations, its use is expected to expand further.

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The solvent generally used is commercial normal hexane with boiling range of 152°F. to 157°F. The industry is well aware of the flammable nature of this solvent. Operators of solvent-extraction plants have adopted stringent procedures and regulations to guard personnel and property against the hazards of fire and explosion.

The lower explosive limit (1) (LEL) of hexane is 1.2% of solvent vapors in air by volume, and the upper explosive limit (UEL) is 6.9%. Such explosive mixtures of solvent vapors and air may occur from a number of causes, such as spills, leaking gaskets, stuffing boxes and seals, incorrect venting, inadequate con-