Some Theoretical and Practical Aspects of Polyester Whitening From the Wash Bath

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Abstract

Uptake of fluorescent whitening agents from aqueous and organic systems by polyester fibers and films under various conditions was investigated. Different factors influencing the correlation between uptake of the fluorescent whitening agents and their performance in laundry liquors are discussed on the basis of the presented data. The results indicate that fluorescent whitening agents normally used for whitening other synthetic fibers can also have valuable additional effects on polyester. Furthermore the results are discussed in terms of the possible mechanisms of whitening.

Introduction

In view of the trend toward higher proportions of polyethylene terephthalate fibers in launderable textile articles, it is relevant to examine how these fibers behave in the wash bath and, in particular, to what extent they can be whitened in the wash bath.

The advent of polyester fibers with their very compact structure created new problems for the textile dyer. These problems have practically all been solved by the use of suitable dyes and high-temperature or carrier dyeing methods. To date much has been written on the mechanism of the dyeing process and the consensus is that polyester fibers can only be dyed satisfactorily at elevated temperatures. For aqueous dyeing systems it may safely be assumed that the dye first goes into solution and then diffuses into the fiber.

This work is an attempt to contribute to the basic understanding of whitening polyester from the wash bath.

Uptake of Fluorescent Whitening Agents by Polyester Films

Preliminary tests to elucidate a number of factors affecting fluorescent whitening agent (FWA) uptake (and hence the whitening) of polyester from aqueous systems were carried out on a simple, readily measurable model consisting of polyethylene terephthalate film. The uptake of FWA by the film was measured spectrophotometrically at the ultraviolet-absorption maximum of the FWA.

Figure 1 shows FWA build-up on polyester film from an aqueous system at boiling temperature. Small amounts of a nonionic surfactant with a low hydrophile-lipophile balance (HLB) value were added to improve the wetting of the hydrophobic film. The uptake of FWA was hardly affected by the addition of this type of wetting agent. The system does not attain a state of equilibrium so that there is good reason to believe that the rate-determining process, i.e., rate of solution of the FWA in the aqueous phase, is very slow. FWA I, 1,2-di(5′-methylbenzoxazolyl-2′)-ethylene, which is slightly water soluble and is present as an extremely fine dispersion in the bath, exhausts only slowly onto the film, even with higher amounts present in the bath.

To increase the amount of dissolved FWA in the system a solvent-based emulsion (benzene in water) has been used where the FWA is dissolved in the solvent phase. As Figure 2 shows the uptake was still slow and the equilibrium had not been attained again after 24 hr. Although the systems described can not be directly compared with each other, it seems that the exhaustion process itself is very slow.

In another attempt to increase the supply of FWA molecules dissolved in the liquor, increasing amounts of alcohol were added to the solvent system used in the tests first described. Figure 3 shows that in this case the distribution equilibrium shifts rapidly in favor of ethanol until the point is reached where in pure alcohol the FWA remains almost quantitatively in solution.

From the shape of the curve in Figure 4 it may be assumed that without a surfactant much of the FWA will be adsorbed on the surface of the film. Wetting agents with detergent properties (high HLB values) induce desorption of the adsorbed FWA component and only the absorbed component is retained by the film, as can very neatly be demonstrated in a wash test under practical conditions.

Whitening Polyester Fabrics From the Wash Bath

The film model gives quantitative information on the uptake of FWA by the substrate. Little information is obtained, however, about visually perceptible whitening effect. The latter is after all the sole decisive criterion for use of FWA under practical conditions. Unlike dyes, FWA are only fully effective when dissolved in molecular form in the substrate. Particle agglomerates and surface deposits may weaken the brightening effect. The

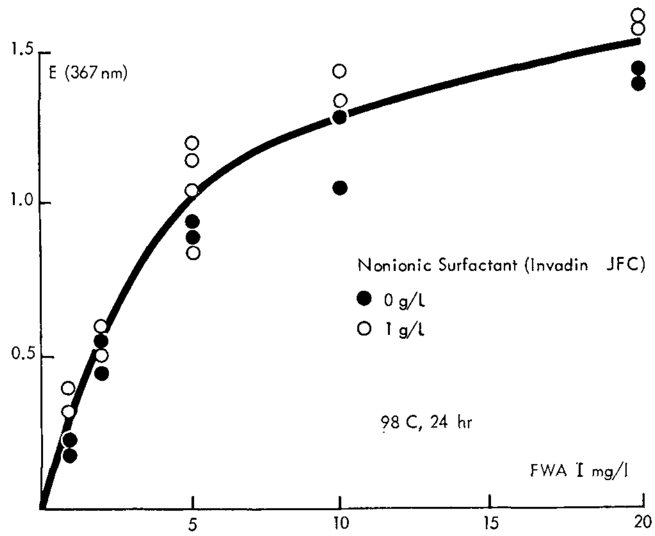

Fig. 1. Absorbancy of polyester films treated with FWA I.

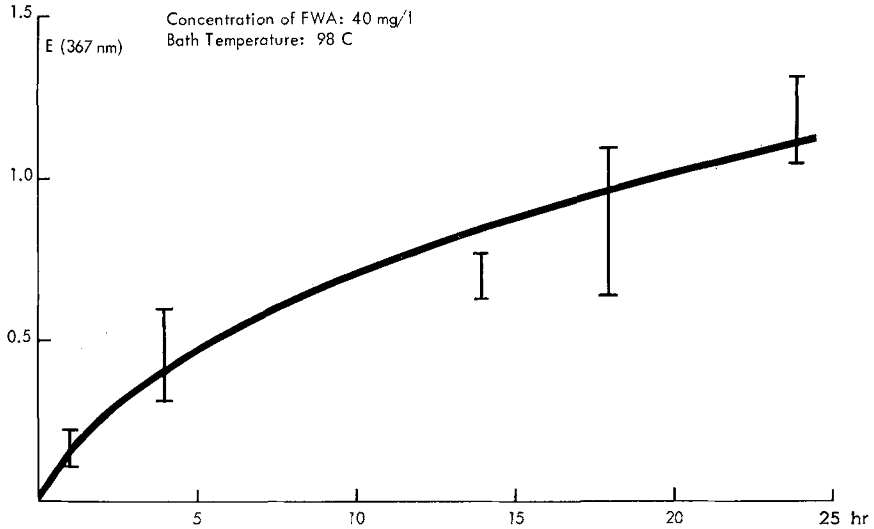

FIG. 2. Absorbancy of polyester films treated with an emulsion of FWA I. FWA dissolved in benzene. Benzene in water emulsion.

natural color of the agglomerated FWA changes the shade of the substrate.

Table I sums up the mean values determined in parallel series of tests. Polyester fabrics were washed according to a standard procedure. FWA II, 2,5-di-(benzoxazolyl-2′)-thiophene, was added to the wash liquor from a stock solution to ensure optimal dispersion. After drying, the pieces of fabric were visually examined, briefly washed with cold acetone and examined again. The concentration of FWA in the acetone was determined spectrophotometrically.

With rising bath temperature the polyester fabric is only slightly whitened in the absence of detergent. Acetone extraction of these pieces of fabric shows that about half the available FWA is deposited on the fiber. Unlevel local deposits of FWA on the fabrics are clearly visible in the fluorescence microscope of the swatches washed in absence of detergent. There are no such deposits on the specimens washed in a liquor containing detergent. This is shown in the fluorescence microphotographs (Fig. 5) in 500-fold magnification on the individual fibrils.

Only very little of the available FWA diffuses into the fiber. The figures in brackets in Table I represent the amount of FWA in the fiber responsible for the visually determined whitening effects and is quoted as a percentage of the original FWA concentration in the wash bath. The calibration curve used (Fig. 6) indicates the maximum effect of FWA II on polyester as a function of the FWA concentration in the fiber when optimally developed.

In the presence of detergent, negligible surface deposition of FWA agglomerates occurs and the whitening effect is more intense. The slight amount of FWA still deposited on the fiber surface (very probably as an even, thin layer) does not interfere with fluorescence. However, it is not ideally dissolved in the fiber so that the white produced falls short of the maximum effect possible with the amount of FWA present. This deposited part of the FWA can be fully developed by heating the swatches in a tumbler at 63–88 C or by ironing the specimens at 150 C as shown in Table II. A significant increase of the whitening effect occurs. Some idea of how the individual components of the detergent influence the deposition of FWA particles may be gained from the

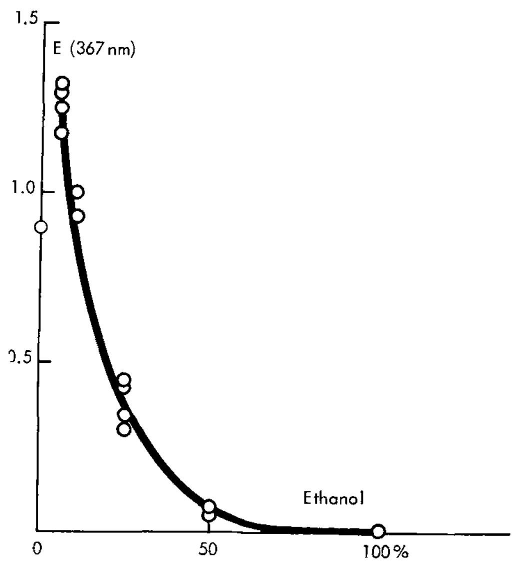

FIG. 3. Absorbancy of polyester films treated with FWA I. Films were refluxed in aqueous ethanol for 24 hr; FWA concentration 4 mg/liter.

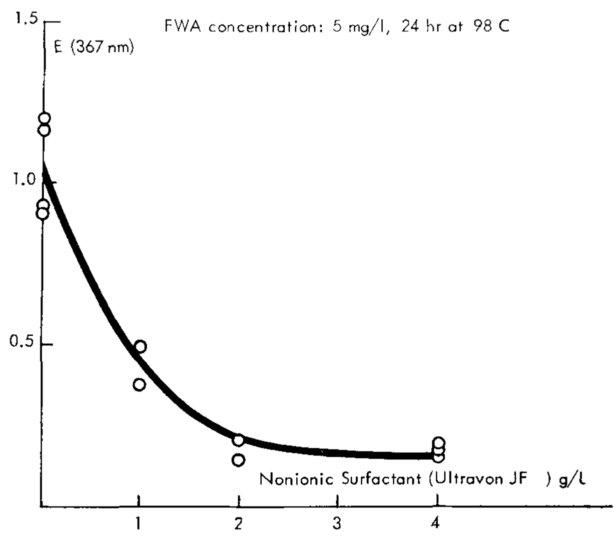

FIG. 4. Absorbancy of polyester films treated with FWA I in aqueous solutions of nonionic surfactants.

TABLE I

Whitening Effect and FWA Deposition on Polyester Fabrics in the Wash Bath

Time: 15 min Liquor ratio: 20:1 Amount of FWA II % o.w.f.	Temperature C	Visual whiteness CIBA white scale extraction with acetone before	 after	Applied FWA removable with cold acetone, %
Without detergent				
0.02	30	95 (2.5)[a]	96 (3)	48
0.02	50	97 (3.5)	98 (4)	43
0.02	70	108 (12.5)	106 (10.5)	42
0.05	30	92 (0.5)	100 (2.4)	43
0.05	50	96 (1.2)	105 (3.8)	48
0.05	70	107 (4.6)	112 (5.2)	51
With 4 g/l detergent				
0.02	30	99 (4.8)	96 (3)	5
0.02	50	104 (8.5)	99 (4.8)	8
0.02	70	113 (18)	106 (10.5)	14
0.05	30	104 (3.4)	99 (1.9)	6
0.05	50	109 (5.2)	103 (3)	5
0.05	70	115 (8)	109 (5.2)	9
Without detergent DBS only builders only with detergent				
0.05	50	95	102	48
0.05	50	100	100	22.3
0.05	50	100	100	26.6
0.05	50	105	100	8

[a] Values in brackets correspond to the effect of optimally developed FWA expressed in per cent of totally applied FWA.

TABLE II

Whitening Effect on Washed Polyester Fabric; Influence of Drying Conditions[a]

Amount of FWA II % o.w.f.	Wash temperature C	Visual whiteness, CIBA white scale, Drying conditions Open air 25 C	 Tumbler, 1 hr 63 C 145 F	 74 C 165 F	 88 C 190 F	 Ironing 150 C 30 sec
0.05	30	100	107.5	107.5	110	107.5
0.05	50	105	107.5	110	115	107.5
0.05	70	117.5	120	120	125	117.5

[a] Wash time, 15 min; liquor ratio, 20:1; DBS detergent, 4 g/l.

final column of Table I. It is interesting to note that builders alone reduce the superficial deposition almost to the same extent as dodecylbenzene sulfonate.

It has been shown in Table II that the whitening effect on washed polyester fabrics is significantly improved by heat treatment in the tumbler or by hot ironing. Units of whiteness of 117.5 and 125 are equivalent to about 9% and 12% respectively of the original amount of brightener in the liquor.

The problems of whitening polyester goods from the wash bath will be apparent from what has been stated so far. Whitening in the wash bath is far more effective on other synthetic fibers such as polyamide and triacetate. Two factors are incontestably responsible for the inferior results obtained on polyester goods, firstly the low solubility of polyester FWA in the aqueous phase of the wash liquor, and secondly the high activation energy required for the FWA molecules to diffuse into the very compact, strongly hydrophobic fiber.

It is apparent from the degree of whiteness versus temperature plots in Figure 7 that strong development of the FWA does not set in below 70 C. The white effect on a fabric treated at low temperatures can be appreciably improved by subsequent heat treatment which causes the FWA deposited on the surface to migrate into the fiber. In textile terminology this process is referred to as thermofixation. Fiber cross sections in Figure 8 illustrate thermofixation at temperatures of 180, 200 and 220 C. In contrast to whitening from aqueous systems, the FWA adsorbed at the fiber surface dissolves in the polyester fiber via the vapor phase (1). Low vapor pressure FWA diffuse at a slow rate and high vapor pressure FWA at a fast rate. The vapor pressure of the latter is so high that at fixation temperatures above 200 C it starts to sublime off the fiber. This effect is already clearly apparent in the center of Figure 8 (arrows) where the boundary zones are deficient in FWA.

Although many attempts have been made to correlate the constitution and whitening power of polyester FWA, the products available at present offer no direct evidence for the existence of defined correlations so that a larger and more systematic study is required. Figure 9 compares a number of polyester FWA and the whitening effects attainable with them on polyester fabrics in five washing cycles. Under conditions applied FWA II, 2,5-di-(benzoxazolyl-2′)-thiophene, gave the highest whitening effects.

Not long ago the question was raised (2) whether the use of such FWA is economically justified since the results on polyester are still only limited. Specific polyester FWA imparting effects of only limited intensity are not altogether economical. But

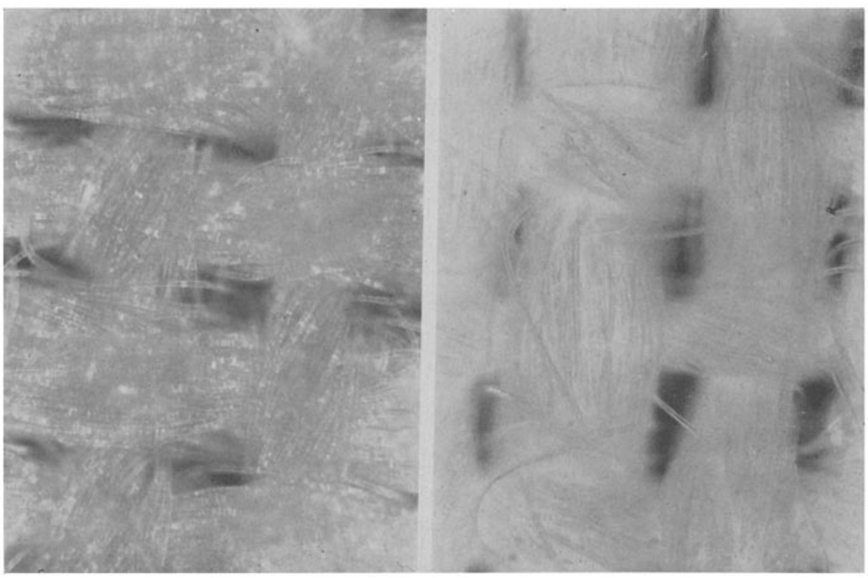

FIG. 5. Fluorescence photomicrographs of polyester fibers. FWA deposition in absence of detergent (left). FWA uniformly distributed in presence of a detergent. No agglomerates (right).

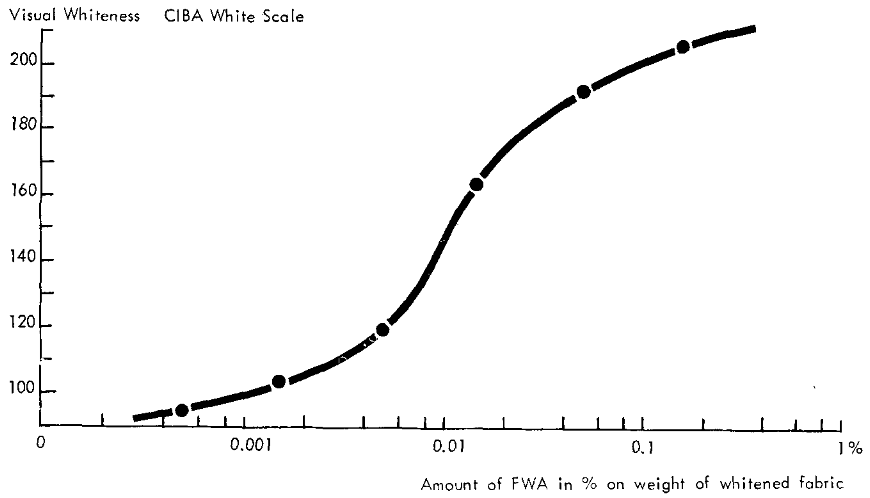

FIG. 6. Relation between FWA effect and concentration for FWA II on polyester fabric.

there are a number of more versatile polyester FWA, such as FWA I and especially FWA II, that can be applied to other fibers such as polyamide, secondary acetate and triacetate from the wash bath, to impart very intense effects with good fastness properties; these are very useful for incorporating in modern detergents. The extra whiteness on polyester would not only preserve the whiteness of the laundered goods through many washing cycles but would often improve it if the goods had only been slightly prewhitened. In the final analysis the lack of undesirable, negative effects such as a tendency to lend a green shade to the substrate through over saturation or stain of the cotton component could count every bit as much as a positive effect. It thus follows that a FWA must always be selected and assessed on the sum of its effects on the laundered items as a whole.

Table III shows the results of a wash and wear test to illustrate the foregoing. Seven shop-purchased, polyester-cotton shirts were laundered after each day's wear with different combinations of FWA. These combinations contained either of two polyester FWA I and III (a styryl-naphthoxazole compound) used in the trade together with the well-known dimorpholino-dianilino-triazinyl-stilbene FWA IV. With FWA I, the effect persists even beyond 30 wash and wear cycles, whereas with FWA III the

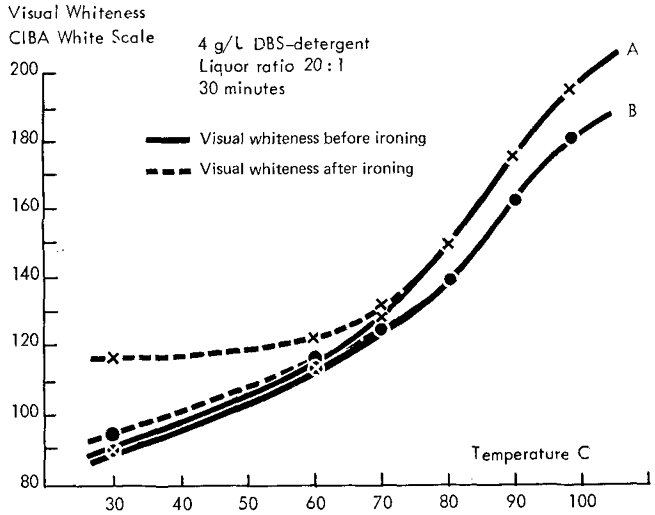

FIG. 7. Polyester fabric whitening with FWA II. A, 0.05% FWA II o.w.f. B, 0.02% FWA II o.w.f.

degree of whiteness diminishes and furthermore the goods have a greenish appearance. The values obtained by visual examination are given alone with the values measured and calculated by the whiteness formula of Berger, Stephanson and Hunter. These latter values also reflect the decrease in degree of whiteness but not the strong shade change towards green.

Materials and Methods

Polymer Film

The polyethylene terephthalate film (Melinex Type O) used was 0.057 mm in thickness. Each piece of film was 3.8 × 7.5 cm in size and weighed 0.2 g. After treatment the film was gently wiped with moist cotton swab and air-dried. Two pieces with a diameter of 20 mm were stamped out of each film for measurement of the extinction E values at 367 nm, the wavelength of absorption maximum of FWA I, $E^{1\%}_{1\,cm} = 1560$. In the first test FWA I was added from a stock solution prepared by dissolving 100 mg of FWA I in 20 ml of dimethylformamide and 80 ml of ethanol. The 0.2 g film was treated in 100 ml of water (liquor ratio 500:1). An oxyethylated 4-octyl-phenol was used as wetting agent.

In the second test (Fig. 2) a stock solution of FWA I was prepared by dissolving 1 g of FWA I in 200 ml of benzene containing 20 ml of emulsifying agent D; 0.8 ml of this stock solution was added to 100 ml of water. For the other tests (Fig. 3 and 4) the stock solution was the same as the one used in

TABLE III
Wash and Wear Test With Men's Shirts[a,b]

Wash and wear cycles	FWA brightener mixture[c]	Visual whiteness CIBA white scale	Values[d] Calculated according to Berger (Y/3 + Z–X)	Stephanson (2Z–X)	Hunter (4B–3G)
New shirts, unwashed		190	44.3	118.0	136
15	1	220	47.8	124.8	152.7
15	2	190g[e]	44.4	117.7	140.5
15	3	190g	45.5	118.9	141.5
30	1	220	46.4	122.6	151.5
30	2	200g	46.1	121.8	150.6
30	3	185g	43.9	117.9	140.4

[a] Polyester, 80%; cotton, 20%.
[b] Washing conditions: DBS-detergent, 1.5 g/l; liquor ratio, 20:1; active chlorine, 0.2 g/l; 50 C, 12 min.
[c] Mixture 1, 0.3% FWA IV + 0.02% FWA I; mixture 2, 0.3% FWA IV + 0.02% FWA III; mixture 3, 0.3% FWA IV + 0.04% FWA III.
[d] Values obtained with Elrepho tristimulus filter photometer.
[e] g, greenish shade.

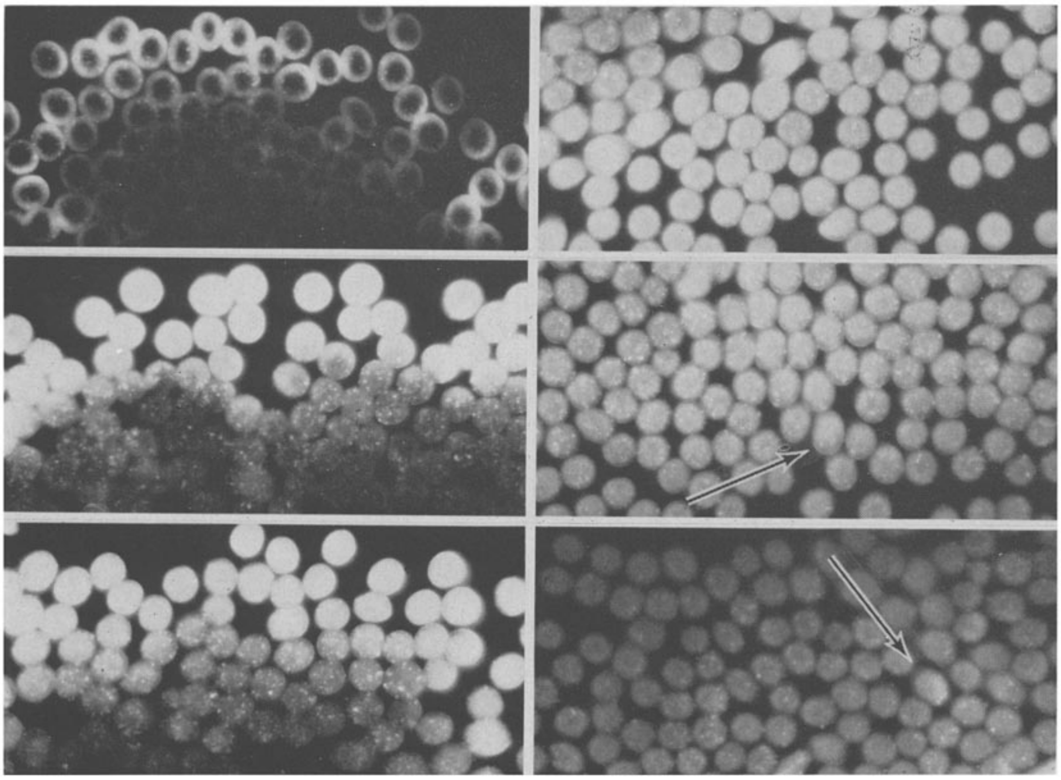

FIG. 8. Fluorescence photomicrographs of polyester fiber cross-sections. Thermofixation at 180, 200 and 220 C for 30 sec. FWA with low vapor pressure (left) and FWA with high vapor pressure (right).

the test first described. Increasing amounts of Ultravon JF nonionic surfactant were added to the test series of Figure 4.

Wash Tests

Tests were run with 10 g samples of Dacron Spun No. 53–302 fabric. Aliquots of a stock solution pre-

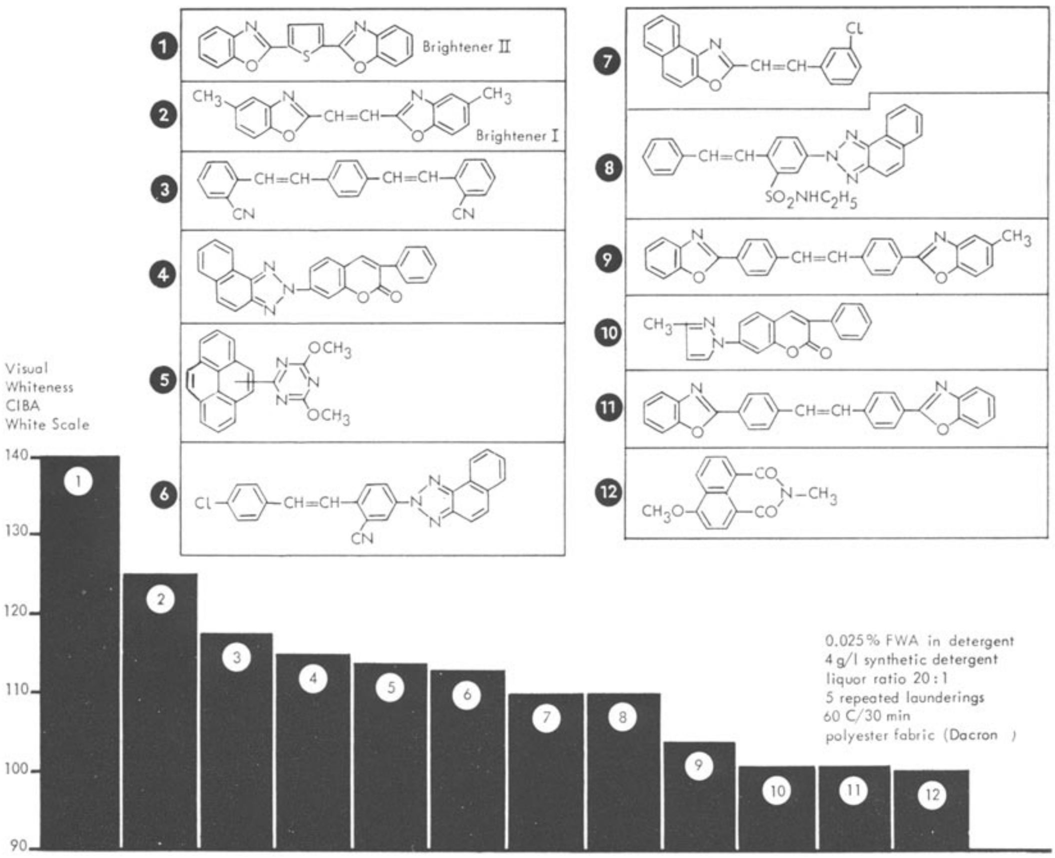

FIG. 9. Whitening effects of typical polyester FWA in the wash bath on polyester fabrics.

pared by dissolving 100 mg of FWA II, 2,5-di-(benzoxazolyl-2′)-thiophene, in 20 ml of dimethylformamide and 80 ml of ethanol were added to the wash liquors. The amount of acetone-extractable FWA was determined by dipping the dried swatches in 200 ml of cold acetone for 5 min. The extinction E of the solutions was measured at the maximum of absorption of the FWA with a Perkin-Elmer spectrophotometer 137-UV. The $E^{1\%}_{1\,cm}$ of FWA I in acetone at 363 nm is 1490. In a separate test it was found that less than 2% of the FWA dissolved in the fiber could be removed by this procedure from polyester fabrics which have been optimally whitened by topical application, i.e., by exhaustion method at 97 C or by thermofixation at 180 C. This indicates that once the FWA has diffused into the polymer it is only eluted to a negligible portion by the acetone treatment described. The whiteness was assessed by visual estimation using the CIBA white scale (3). The whiteness of the untreated fabric was 90 units. The figures in Table I represent the average values of three parallel runs. The detergent used consisted of 10% of dodecylbenzenesulfonate, 30% of sodium tripolyphosphate, 3.3% of anhydrous sodium metasilicate, 10% of anhydrous sodium carbonate, 44.7% of anhydrous sodium sulfate and 2% of carboxymethylcellulose.

For the wash and wear test, European men's shirts without a permanent press finish were used. The FWA were incorporated into the slurry of a standard DBS detergent which was spray dried. The detergent, the wash load and the NaOCl were added to the wash bath in this order.

ACKNOWLEDGMENT

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