The Use of Optical Brighteners for Synthetic Fibers in Detergents¹

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Abstract

It has been demonstrated that the choice of the right optical brightening agent for use in the dope or for topic-brightening in the textile-mill has a big influence on the ability of the fiber to be further brightened in the wash-bath, on the lightfastness and the washfastness of the white, and very often also on the colored washload. The investigation also deals with the mutual influence of brighteners applied during the production of the fiber or the fabric and those used in detergents. Ways are described to overcome undesired changes in the hues of pastel shades. Some aspects of the visual assessment and measurement of whitening effects are discussed.

Introduction

Looking at the production figures and the production forecast of textile fibers it can clearly be seen that, although cotton will maintain a very strong market position, the part of synthetic fibers in overall textile production is increasing very strongly. It has been calculated that in the period between 1961 and 1975 the yearly growth rate will be 14.4% for synthetic fibers, compared with 1.1% for cotton.

A second factor which has to be observed is the fact that a large proportion of all fibers, especially synthetics, are brightened before coming on the market. In 1964 for example 15.4% of the produced synthetic fibers had already been treated with optical brighteners on leaving the mill. In the sector of white textile goods which today come on the market practically all have been treated with brighteners. These factors today make the brightening of synthetics in the washing process increasingly more important and also more complex. The reasons for this can be found in the fact that the type and manner of prebrightening influences more strongly the behavior of synthetics in the wash load than is the case with prebrightened cotton. With the help of the fol-

¹ Presented at the AOCS Meeting, Chicago, October 1967.

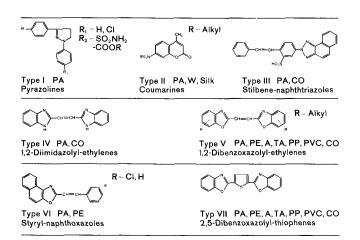


FIG. 1. Brighteners for synthetic fibers in detergents.

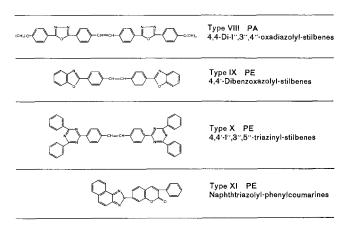


FIG. 2. Some major brighteners for synthetic fibers, dope brightening.

lowing few examples some of these relationships, especially on polyamide and polyester, will be discussed.

Structures of Brighteners for Synthetic Fibers

In order to have a better survey over these interrelations the structures of some typical brighteners which are applied for these fibers in detergents, in the dope and in the textile wet finishing process are compiled.

Brighteners for use in detergents are shown in Fig. 1: pyrazolines (type I) and the coumarins (type II) which are destroyed in the wash bath containing active chlorine, and the types stable to chlorine such as the stilbene-naphthotriazoles (type III), diimidazolyl-ethylenes (type IV), dibenzoxazolyl-ethylenes (type V), styryl-naphthoxazoles (type VI) and the dibenzoxazolyl-thiophenes (type VII).

Some major brighteners for dope brightening of polyamide and polyester are compiled in Fig. 2. They have the following structures: oxadiazolyl-stilbenes (type VIII), dibenzoxazolyl-stilbenes (type IX), triazinyl-stilbenes (type X) and the naphthotriazolylphenylcoumarins (type XI).

A third place where optical brighteners can come

Type XII (VII) PE, PA, PP, A, TA. PVC Type XIII PA H, t-Butyl, Cumyl Triazinyl-diamino-stilbene-2,5-Dibenzoxalyl-thiophenes disulfonicacid salts Type XV PE, PA, PVC Type XVI PE Type XIV PE, PA Alkyl CN in 2' or 4'-position 1,8-Naphthalimides Stilbene-naphthtriazoles 1,4-Distyryl-benzenes

FIG. 3. Some major brighteners for synthetic fibers, topical application and dope brightening. A, acetate; CO, cotton; PA, polyamide; PE, polyester; PP, polypropylene; PVC, polyvinylchloride; YA, triacetate; W, wool.

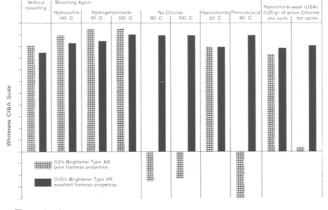


FIG. 4. Fastness to bleaching agents of brighteners Type VII and XIII.

into contact with the synthetic fibers is in the textile wet finishing process. Products mainly of the following structures are applied (Fig. 3): 2,5dibenzoxazolyl-thiophenes (type XII and type VII respectively), triazinyldiaminostilbene-disulfonic acid salts (type XIII), derivatives of distyrylbenzene (type XIV), 1,8-naphthalimides (type XV) and the stilbene-naphthotriazoles (type XVI). Some of these brighteners are well suited for dope-brightening.

Attention should especially be drawn to the fact that type VII is in many ways an ideal optical brightening agent for synthetics. This is because its development enabled the possibility of using this optical brightening agent (OBA) for a dual application in both the textile mill and in household detergents. In this way the use of OBAs which do not harmonize with each other is avoided.

Influence of Different Fiber Pre-brightening on the Brightener Performance in the Wash Bath

In the next few examples it is shown what may happen if the OBAs used in different applications, such as dope, textile mill, detergent, are not wisely chosen.

The brightener can be adversely affected by numerous factors such as light, bleaching agents or wash-

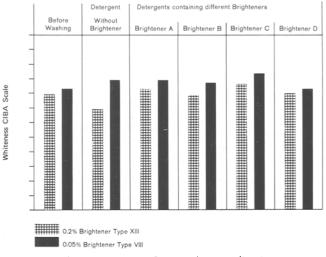


FIG. 5. Fifty repeated launderings (60 C/15') with exposure to daylight in the wet stage after every cycle.

ing conditions. It can not only be destroyed but also degraded into colored degradation products. Very often the discoloration of the fabric is irreversible and withstands repeated wash cycles with detergents containing brighteners. During the course of an investigation of the effect of various bleaching operations on the dope-brighteners type VIII and XIII, we found the following (Fig. 4). The hypochlorite bleach caused some damage to type XIII while the sodium chlorite and peracetic acid bleach completely destroyed type XIII. This caused a yellowing of the polyamide material. It is especially interesting to note that after 10 cycles of a normal hypochlorite treatment in the washing process type XIII OBA was remarkably damaged. On the other hand, type VIII OBA was not attacked by any of the bleaching operations described nor was the lightfastness adversely affected. This is a good illustration that the brightening effect obtained during the wash process is not dependent solely upon the OBAs present in the wash solution.

The behavior of the two dope brighteners types VIII and XIII after 50 repeated launderings is

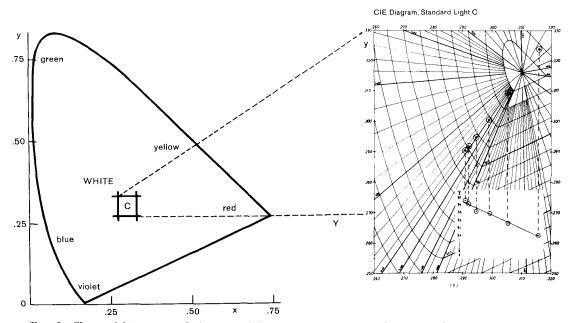


FIG. 6. Chromaticity plots and lightness (Y) values of brightened (Type VIII) polyamide fabric.

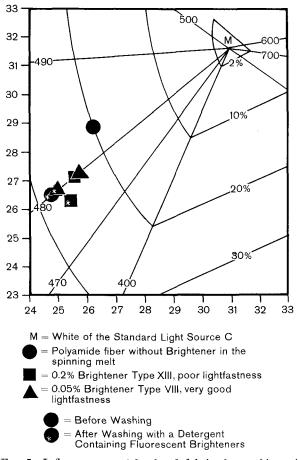


FIG. 7. Influence on pastel colored fabrics by washing with a household detergent containing fluorescent brighteners. Section of the chromaticity diagram of the CIE-System.

illustrated in Fig. 5. During these experiments the polyamide swatches were allowed to dry by exposure to air between each wash cycle. In this way the influence of light and dust during the drying period which lasted a few hours was deliberately not avoided. For the purpose of these tests, detergents containing different types of OBA for synthetic fibers were used. The results show that in these tests the dopebrightener type VIII gave better results and that it was much less affected by the detergent brighteners. A(stilbene brightener), B(coumarin brightener), C(stilbene brightener) and D(benzoxazolyl brightener).

In the event that the wash load contains some fabric dyed in pastel shades the resulting change in shade can be a frequent cause of complaint. This fact has often led to claims where the blame has, quite wrongly, been attributed to the washfastness of the dyestuff. In most cases this change in shade is caused by the brightener in the detergent, which brightens the colored but not pre-brightened fabric. As a result of this Mecheels et al. (1) have suggested that UV absorbers should be used in combination with dyestuffs, to improve the lightfastness of the color, as well as to avoid the change in shade which might result from household detergents which contain OBA. In the case of woven goods or printed materials the effect of UV absorbers would be limited to the colored areas and in this manner the OBAs in the detergent would be available for use in the noncolored areas of the fabric.

In our opinion this problem can be solved more elegantly if the colored fibers are pre-brightened in Influence of the Brighteners on the lightfastness of colored Fibers (Polyamide 6 dull)

| | Pastel Shade with 0.1% Tectilonblue R | Standard Shade with 3% Tectilonblue R |
|-----------------------|---|---|
| Without Brightener | 5-6 | 6 |
| 0.2% Brightener XIII | 3-4 | 5-6 |
| 0.05% Brightener VIII | 5-6 | 6 |

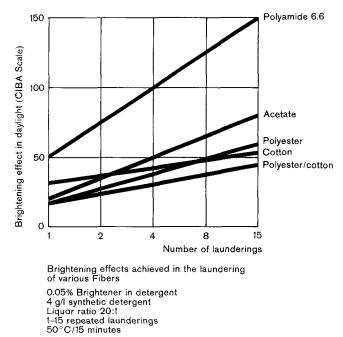
Xenotest exposure

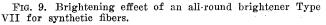
FIG. 8. Brighteners Type VII and Type XIII in dope dyed polyamide.

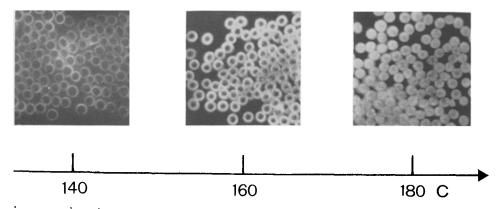
the textile finishing process or in the dope with a suitable brightener. The brightener should have a neutral shade and should not show any tendency to discolor the fabric at higher concentrations. As shown in Fig. 6 the brightener type VIII behaves in this regard almost ideally. The values of increasing concentrations in polyamide lie on the same dominant wavelength (470 μ M) in the standard CIE 1931 chromaticity system.

We have found that in this manner purer and more brilliant shades result. In addition to this it can be seen in Fig. 7 quite clearly that the difference in shade of pastel colors, observed after washing with detergents containing brighteners, is much smaller than with polyamide which is not pre-brightened. In this way a change in shade by household detergents can be avoided. Figure 8 once more demonstrates that in the case of dope brightening the choice of suitable OBAs is of importance for the quality of the finished product. While the brightener of type XIII deteriorates the lightfastness of pastel shades as well as of normal colors, the good lightfastness values of the dyestuff remain completely unaffected if a brightener of type VIII is applied.

With these few examples it has been demonstrated that it is very important to regard the brightening process, beginning with the dope brightening of synthetics and ending with the brightening in the wash bath, as one complete process consisting of different mutually interacting steps. In all stages where OBAs







increasing temperature

Fig. 10. Brightening process of a polyester fiber by topical application cross-sections of a PE-fiber fluorescence microscope (150:1).

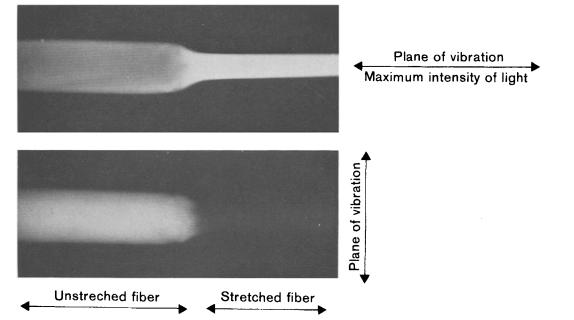


FIG. 11. Ultraviolet-dichroism and polarization of the fluorescence light. Polyester-fiber, dope-brightened, concentration of optical brightener: 0.02%. Observation in the fluorescence microscope (300:1) fiber illuminated with polarized ultraviolet light.

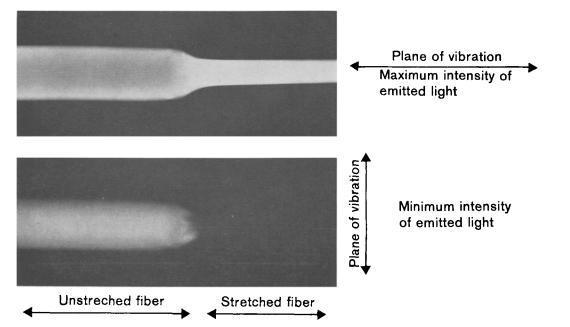
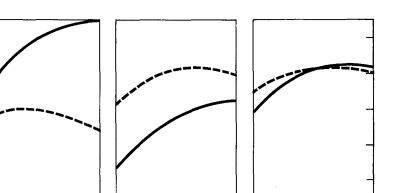


FIG. 12. Ultraviolet-dichroism and polarization of the fluorescence light. Polyester-fiber, dope-brightened, concentration of optical brightener: 0.02%. The fluorescing fiber observed through a polarization filter, the fiber is illuminated by unpolarized light. (300:1).



Concentration on the fabricConcentration on the fabricConcentration on the fabricBrightener EBrightener FBrightener G

———Brightening effect evaluated at daylight (CIBA White Scale)

FIG. 13. Fluorescence number and whiteness by visual evaluation of topical brightened polyamide.

are applied it is absolutely necessary to use products with good properties under the conditions of practical use.

Whiteness CIBA Scale/Fluorescence number

250

200

150

100

50

It is clearly advantageous if one can use an optical brightening agent of type VII which has the ability to be used in different applications such as wet finishing and in household detergents. Incidentally type VII is in fact the most widely used brightener in the textile wet finishing especially for polyester. By these means possible adverse interactions of brighteners having different structures are avoided.

A good brightener for synthetics in detergents should possibly have effects on all types of fibers which can be found in the wash load. Brightener VII has this property to brighten in the wash bath polyamide, acetate, triacetate, polypropylene polyvinyl-chloride and to a certain degree also polyester and cotton (Fig. 9). This additional effect on polyester is especially worthwhile because the brightening of this type of synthetic fiber is an extremely difficult problem. There is evidence that the brightening of the highly lipophilic and very compact polyester fiber is working according to a different process than the dyeing of polyester fibers with dispersed dyes, which was investigated by Milićević et al. (2). Figure 10 shows the course of brightening of the polyester fiber by topical application. The brightener deposited on the surface of the fiber has then to be dissolved completely in the polyester fiber at elevated temperature

| | % Active Ingredient | Whiteness CIBA-White-Scale | FluorescenceNumber |
|--------------|------------------------|-------------------------------|--------------------|
| Control | | 0 | 4 |
| Brightener A | 0,015 | 135 | 160 |
| | 0,030 | 165 | 191 |
| | 0,060 | 170 | 200 |
| Brightener B | 0,015 | 95* | 185 |
| | 0,030 | 95* | 210 |
| | 0,060 | 100* | 230 |

*Pronounced greenish shade

Washi

| ng Condition: | Detergent | 4 g/l |
|---------------|-----------------|------------|
| | Chlorine active | 0,25 g/l |
| | Liquor Ratio | 1:20 |
| | Temperature | 50 C |
| | Time per Cycle | 15 Minutes |
| | | |

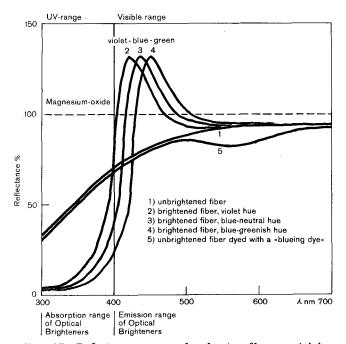
FIG. 14. Fluorescence-numbers and whiteness of polyamide fabrics after 50 repeated launderings.

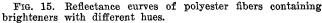
in order to develop fully its fluorescing properties. In this connection it is interesting to note the marked ultraviolet-dichroism and the strong polarization of the fluorescence light in the stretched polyester fiber which has been dope-brightened (Fig. 11 and 12). The mechanism of brightening the polyester fiber at lower temperature (20-95 C) in the wash bath is currently being studied.

Having discussed a few aspects of mutual interactions between brighteners applied in the different processing stages and also some fundamental properties an ideal brightener for synthetics should possess, a few remarks on the problem of the measurement of whiteness are added.

Some Aspects of Whiteness Control

A method which is very often used to compare the brightening effects of different brighteners is the determination of the fluorescence number. This is valid only within very strict limits. Figure 13 shows





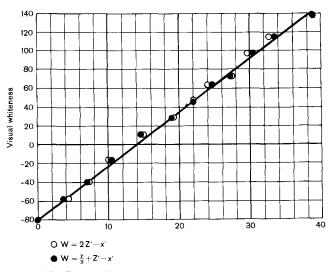


FIG. 16. Correlation between the visual evaluation with the CIBA white scale and the values measured and calculated with the formulas according to Berger (\bullet) and Stephanson, resp. Harrison (\bigcirc) .

the degree of whiteness which was obtained on polyamide by the application of different brighteners for synthetics. In one instance the degree of whiteness was measured by fluorescence number and in the other by visual evaluation. The comparison shows clearly that the values obtained by measuring the fluorescence number are not always parallel to the values determined by visual evaluation if a range of concentrations is compared. A second conclusion of this investigation is that one can not compare fluorescence numbers of one brightener with one of a different structure. Measurements of fluorescence numbers have therefore only limited practicability. They are not suitable for comparing measurements of whiteness but can be useful for other purposes such as quality control. A further example of this fact is illustrated in Fig. 14. Polyamid fabrics were washed 50 times with normal household detergents containing two different brighteners, A and B respectively. It can clearly be seen that neither the strong fall in whiteness nor the true change in shade can be registered by the determination of the fluorescence numbers which do not correlate with the values of the visual evaluation.

A good way to detect changes in shades by measurement is the recording of the reflectance curves. Figure 15 shows the reflectance curves of polyester fibers containing brighteners with different hues. The maximum remission of a violet brightener usually is between 420–430 μ M, of a blue brightener 435–440 μ M and of a green OBA 440-450 μ M.

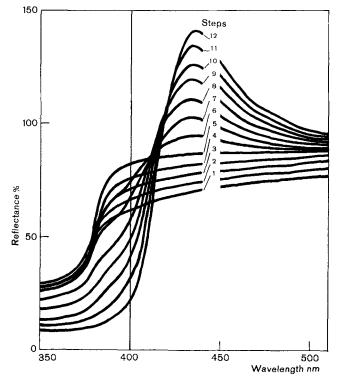


FIG. 17. Reflectance curves of the cibanoid white scale,

Due to the fact that today no procedures for the measurement of the degree of whiteness are internationally defined and that satisfactory units of a white scale do not yet exist, a new white scale has been developed in our laboratories. This scale, made from plastic, is lightfast and washable and shows a good correlation with a number of established whiteness formulaes (Fig. 16). Figure 17 shows the reflectance, and the fluorescence superimposed upon it, of the new Cibanoid white scale. Steps 1 to 4 contain decreasing quantities of a lightfast yellow pigment, step 5 contains neither pigment nor brightener, and steps 6 to 12 contain increasing quantities of a very lightfast brightener. Details of the new white scale and the problems of measurement of white have recently been described by Anders (3).

ACKNOWLEDGMENT

N. Bigler made the microscopic studies on brightened polyester fibers; G. Anders and K. Kleiber gave technical assistance.

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- [Received May 20, 1968]