

Kinetics of Staining and Bleaching

Erik Kissa*, Jenny M. Dohner, Ward R. Gibson and Donna Strickman

Jackson Laboratory, Chemicals and Pigments Department, E.I. DuPont De Nemours and Company, Wilmington, DE 19898

Kinetics of staining and stain removal have been studied with food dyes and natural colorants. Kinetics of staining indicate that the staining agent is adsorbed on the fiber surface and diffuses into the interior of the fibers. Similarities exist between staining and dyeing mechanisms of cotton, polyester and nylon fibers.

Stain removal by nonoxidative detergency involves diffusion of the staining agent from the interior of fibers and desorption from the fiber surface. The kinetics of stain removal by bleaching with peroxyacids or activated sodium perborate depend on the affinity of the stain to fibers. When desorption of stain is rapid, bleaching of the stain in solution is the rate-determining step and stain removal obeys pseudo-first-order kinetics.

When the stain is washfast, the concentration of the stain in fibers decreases with the square root of time, indicating a diffusion process. The peroxygen bleaching agent is sorbed in the subsurface of fibers or diffuses into the interior of fibers. If bleaching occurs in the outer perimeter of fibers, the rate-determining step may be the diffusion of stain molecules from the interior of fibers to the location of the bleaching agent. On the other hand, if bleaching occurs within fibers, the rate-determining step may be diffusion of the bleaching agent to the stain located within the fibers.

KEY WORDS: Bleach activators, bleaching, cotton, determination stain, food dyes, kinetics, mechanisms, natural colors, nylon, peracetic acid, perhydrolysis, polyester, sodium perborate.

Stain is a discoloration caused by intensely colored substances, which in small amounts can affect the color and appearance of a textile. Commonly, the term stain denotes either a staining agent or the resulting discoloration, which needs a bleaching agent or an enzyme for its removal. From a physical-chemical point of view, it is useful to distinguish between stains and soils. A soil on a fabric constitutes a separate phase—a liquid, a semisolid or a solid. In contrast, a stain is usually caused by molecules of colored substances deposited on or in fibers or in residual soil. The term stain implies a degree of permanency not necessarily associated with soil (1). Common stains are (1–4) natural colors; synthetic food colors; substances of biological origin, such as blood and proteins; pigments; and oxidation products of residual soil or antioxidants.

Stain removal depends on the physical state and location of stain and, consequently, on staining conditions. An understanding of staining mechanisms is therefore essential for developing stain-resistant finishes, bleaching systems and stain removal tests.

Bleaching is one of the most important aspects of the detergent field, and is subject to changes. Chlorine-based bleaching agents are being replaced by peroxygen bleaches (5,6). The driving forces are environmental restrictions, compatibility with detergent formulations, inertness to

textile dyes and consumer preferences. The peroxygen bleaches have some limitations, however. Hydrogen peroxide, released by sodium perborate or sodium percarbonate, is not sufficiently active at low washing temperatures. Catalysis with metal salts (7,8) is difficult to control and may be environmentally unacceptable. The more practical alternative is to convert hydrogen peroxide to a peroxyacid. While preformed peroxy-carboxylic acids (5,9–15) still await commercial acceptance, peracids generated by a “bleach activator” in the detergent solution are in commercial use (5,6,8,16–21).

Bleaching in solution has been shown to obey pseudo-first-order kinetics (13). However, the kinetics and mechanisms for bleaching of stain residing in fibers are not sufficiently understood. Bleaching kinetics are complicated by the simultaneous existence of two processes—stain removal by nonoxidative detergency and oxidative destruction of stain. Bolsman and co-workers (13) investigated the decomposition and bleaching reactions of long-chain peroxy-carboxylic acids. Their systematic and thorough study found concurrent stain removal by the detergent and by bleaching to obey third-order kinetics (13). However, stain removal by bleaching, although significant, is small relative to the amount of stain removed by nonoxidative detergency (Fig. 1). The overall soil removal rate, including both bleaching and nonoxidative detergency, does not unequivocally define the kinetics of bleaching.

Both processes have to be investigated separately to differentiate between mechanisms of bleaching and nonoxidative detergency. Therefore, we simplified the bleaching process by i) using chopped fibers to reduce the effect of fabric geometry and ii) washing stained fibers before kinetic measurements to detach stain removable by nonoxidative detergency.

EXPERIMENTAL PROCEDURES

Materials. Cotton yarn (40/2 cotton skeins, Testfabrics, Inc., Middlesex, NJ) was immersed in 5% NaOH, containing 0.01 g/L Mersol SE, a nonionic surfactant, at the boil for 30 min. The yarn was neutralized with hydrochloric acid and washed acid free with water. Spun Dacron, Type 54, polyester yarn and nylon-6,6, Type 1500 Superba heat-set yarn were extracted with petroleum ether. The yarn was cut to 2-cm long pieces before staining.

The chemicals were either purchased from Aldrich Chemical Co. (Milwaukee, WI) or prepared in Du Pont laboratories (Wilmington, DE).

Procedures. Bleaching in solution was measured at ambient temperature (24°C) by using a Hewlett-Packard Model 8450A diode array double beam spectrophotometer (Hewlett-Packard, Palo Alto, CA).

Chopped yarn was stained with natural or synthetic food colors. The stained yarn was washed in a Terg-O-Tometer (U.S. Testing Co., Hoboken, NJ) at 50°C with a solution containing 2.5 g/L of sodium pyrophosphate and 0.01 g/L Mersol SE to remove stain deposited on the fiber surface, rinsed with water on a Buchner funnel and

*To whom correspondence should be addressed.

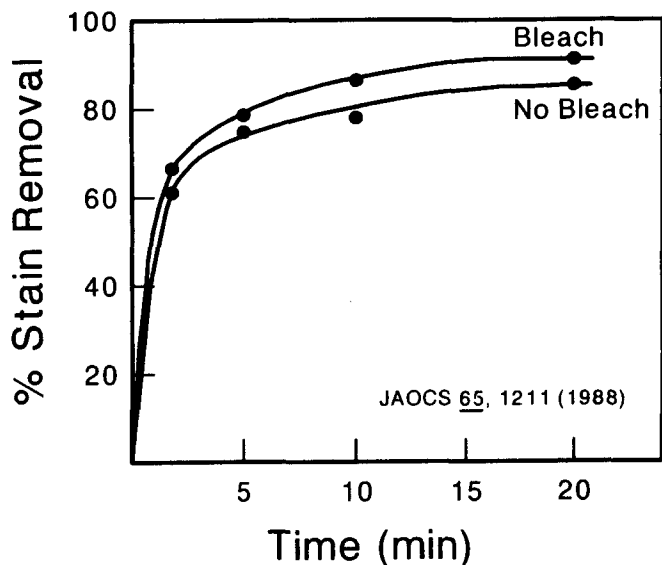


FIG. 1. Bleaching of tea on cotton with and without *n*-pernonanoic acid (data from Table 1, ref. 13).

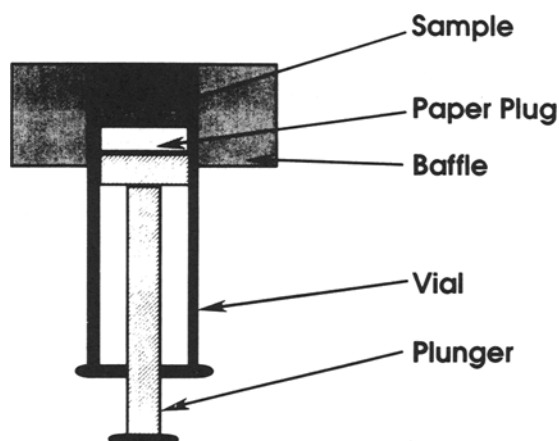


FIG. 2. Sample holder for small samples of chopped yarn.

allowed to dry. Bleaching was done in a shaker bath (American Scientific Products, Inc., McGraw Park, IL) kept at 25, 40 or 55°C, agitation rate 125 strokes/min.

Stained yarn (0.5 g) was immersed in 80 mL of a solution containing the peroxygen bleaching agent [peracetic acid or sodium perborate activated with sodium nonanoyloxybenzenesulfonate (NOBS)], an alkaline buffer and a nonionic surfactant (0.01 g/L Mersol SE). The components of the solution were equilibrated individually and mixed immediately before adding stained yarn. The volume/fiber ratio was kept large to maintain a reasonably constant oxidant concentration and facilitate the liquid/fiber contact. At the end of the bleaching time interval the yarn was removed from the solution, dropped into 200 mL of water and stirred. The yarn was then placed into a barrel of a 10-mL syringe, squeezed dry in the syringe and allowed to dry in air at ambient temperature.

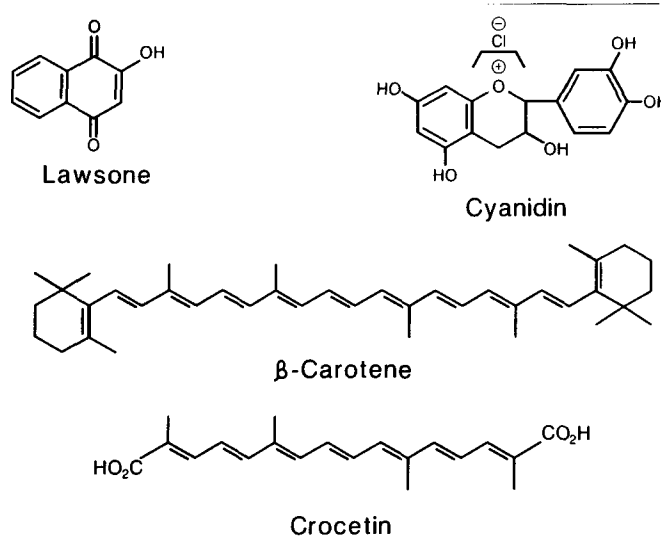


FIG. 3. Examples of natural colors.

The color of the yarn was measured in the $L^*a^*b^*$ color space with a Minolta Model CR-200 chromameter and recorded as ΔE values. Because the amount of yarn used for each time interval was small, we designed a special sample holder (Fig. 2). The yarn was placed into a flat-bottomed 22 × 90 mm vial, equipped with a TS19/22 female joint. Four rubber rings (2.5" OD × 0.5" thick with a 0.75" hole, Bevco Industries, Inc., Aston, PA) served as a baffle. The yarn was covered with a plug made of soft paper and compressed with a plunger taken from a 10-mL plastic syringe. The plunger was relaxed and the color read through the bottom of the vial.

In some kinetic runs the residual stain in fibers was determined also by extraction of the stain and transmission spectroscopy. The extraction methods used have been published before (22). An apparently linear correlation between the stain content, determined by extraction, and the ΔE values, obtained by reflectance measurements, was established for residual stain.

RESULTS AND DISCUSSION

Staining. The intensity of stain depends on the nature of the fibers and the chemical composition of the staining substance.

Most natural colors are nonionic and do not dissociate in water. Some natural colors are ionic and, in water, can form negatively or positively charged colored ions (Fig. 3). All synthetic food colors have sulfonic or carboxylic acid groups and are therefore anionic (Fig. 4).

Staining with natural colors or synthetic food colors is similar to dyeing with textile dyes. The staining propensity depends, in analogy to dyeing, on the affinity of the staining substance to fibers. Affinity depends on the structure of the staining colorant and the nature of the fibers. This is illustrated in Table 1 with cotton, nylon-6,6 and polyester fibers.

Nylon is stained by nonionic and ionic colorants, but nonionic stains in general are easier to remove by aqueous detergents. Synthetic food colors behave like acid dyes.

SURFACTANTS & DETERGENTS

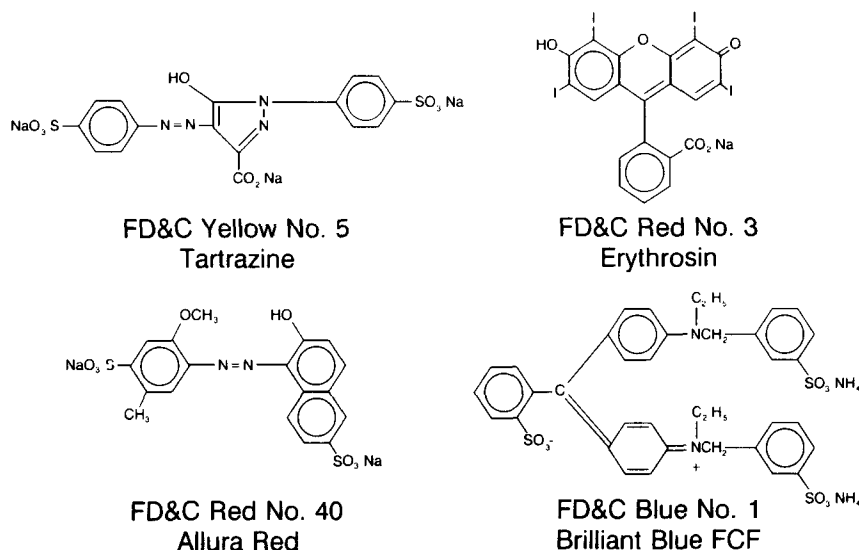


FIG. 4. Examples of synthetic food colors (FD&C Yellow No. 5 = C.I. Food Yellow 4; FD&C Red No. 3 = C.I. Food Red 14; FD&C Red No. 40 = C.I. Food Red 17).

TABLE 1

Staining with Natural Colors and Synthetic Food Dyes

Dye ^a	Dye type	Stain (ΔE) ^b		
		Cotton	Nylon	Polyester
A. In water				
Lawsone (Henna)	Nonionic	6	36	1
Saffron	Nonionic	30	21	2
Tartrazine (F&D Yellow 5)	Anionic	6	40	1
Erythrosin (F&D Red 3)	Anionic	7	35	8
Allura Red (F&D Red 40)	Anionic	6	30	2
Safranine O	Cationic	36	42	10
B. In 005N citric acid				
Tartrazine (F&D Yellow 5)	Anionic	11	46	1
Erythrosin (F&D Red 3)	Anionic	24	57	36
Allura Red (F&D Red 40)	Anionic	21	46	6

^aThe initial absorbance of dye solutions was 1.0. Chopped yarn (0.50 g) was immersed in 20 mL of dye solution at 25°C for 24 hr. During the first two hours of immersion, the solutions in vials were agitated by end-over-end rotation on a rotator (Cole-Parmer Roto-torque rotator).

^bThe stained chopped yarn was rinsed with 20 mL of water for 10 min (agitated on the rotator).

They are sorbed on nylon very intensively and the stain is more difficult to remove with detergents than nonionic stains. An acid, such as citric acid present in beverages, increases staining of nylon. The effect of acidity on staining is similar to that on sorption of acid dyes in nylon.

Synthetic food colors and other ionic colorants have no affinity to polyester fibers and can be removed by detergents. Erythrosin, although a synthetic food dye, stains polyester. This apparent exception can be explained by conversion of erythrosin to its nonionic lactone form during staining in an acid medium. Nonionic colorants do not stain polyester fabrics at ambient temperature but diffuse into polyester fiber at a higher temperature and are then very difficult to remove. Cotton is stained by cationic and nonionic stains. Synthetic food dyes in a neutral

medium stain cotton only slightly, but acidity enhances staining markedly.

Nonionic colors dissolved in an oily or fatty medium can stain polyester, nylon and cotton as well. However, the stain is located in the fatty or oily deposit on fibers and can be removed together with the fatty or oily soil, unless driven into fibers by heat.

Staining can occur by one of the two transport mechanisms—transfer of stain from a soiled substrate to the initially clean substrate or a direct deposition of the staining substance to the fabric (4). A liquid dropped onto a fabric spreads on the fabric by capillary sorption (4,23). Spreading depends on the wettability of fibers by the staining liquid. A colorant in the liquid can be sorbed by fibers, if the colorant has affinity to fibers and the

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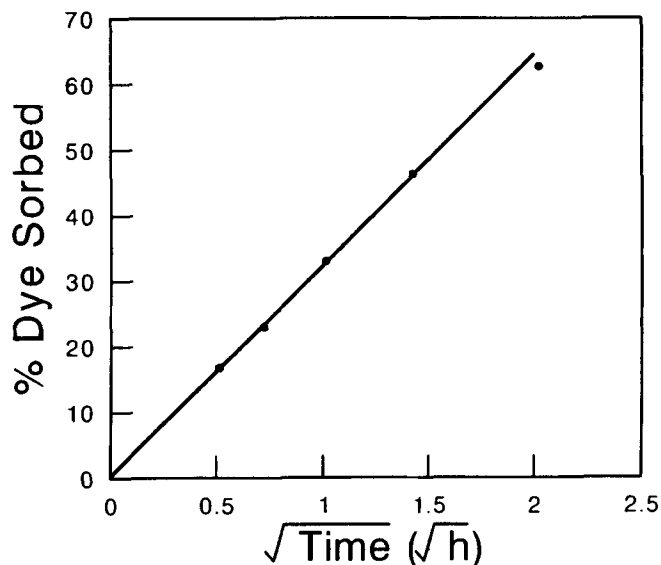


FIG. 5. Sorption of F&D Red 40 on nylon-6,6 Type 1150 yarn at 25°C as a function of square root of time.

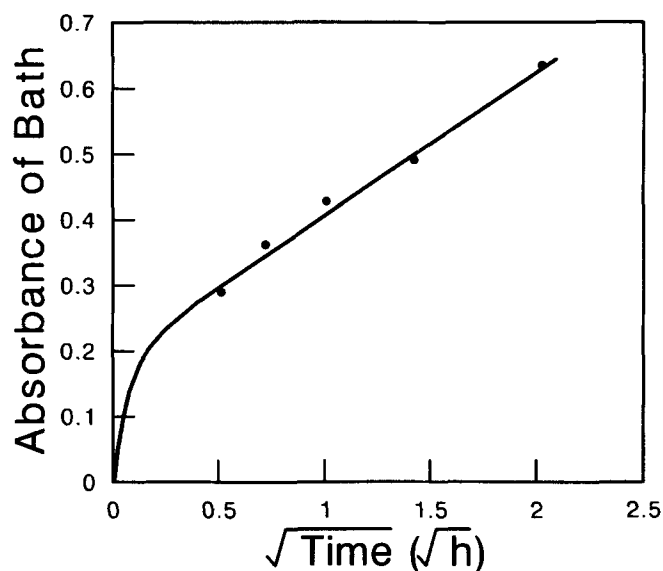


FIG. 6. Desorption of F&D Red 40 from nylon-6,6 Type 1150 yarn in a solution containing 0.0057 M sodium dodecylbenzenesulfonate and 0.05 M sodium carbonate at 25°C.

diffusion rate is adequate. This is illustrated in Figure 5 for a synthetic food dye on nylon. The amount of the colorant sorbed increases with the increasing square root of time, in accordance with Crank's diffusion law (24).

Desorption of stain. The difficulty in stain removal by detergents depends on the solubility of the stain and the location and affinity of stain in fibers. Water-soluble stain with no affinity to fibers is desorbed by a pseudo-first-order process, like other detergative processes with water-soluble soil (4). However, the desorption of stain located in the interior of fibers involves outward diffusion of the

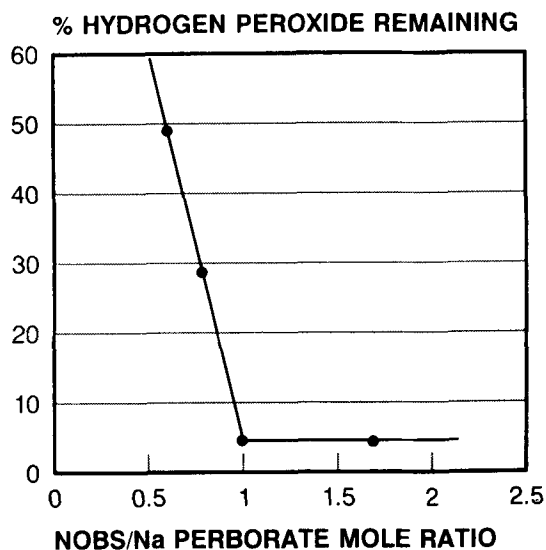


FIG. 7. Perhydrolysis of NOBS in 0.05 N NaOH containing sodium perborate (0.0064 M). Conversion of hydrogen peroxide in 10 min at 25°C, pH 11.9.

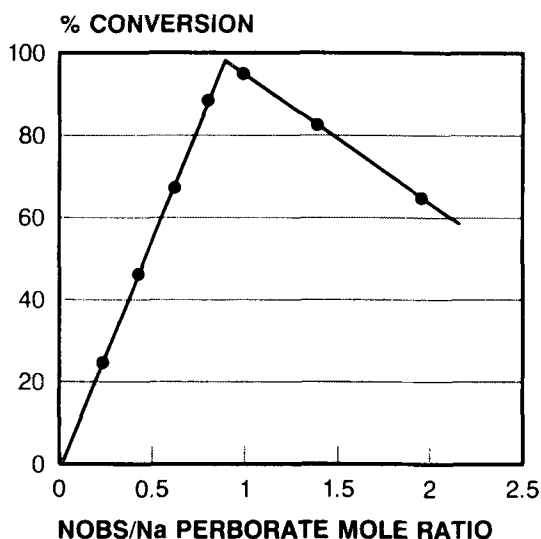


FIG. 8. Perhydrolysis of NOBS in 0.05 N NaOH containing sodium perborate (0.0064 M). Reaction time was 10 min at 25°C. Yield of peroxynanoic acid as a function of the NOBS/SPB mole ratio.

colorant into the detergent bath. This is evidenced by the desorption rate of a food color (Fig. 6). The stain located on fiber surface is removed rapidly. The desorption of stain from the inside of the fibers is slower and proportional to the square root of time, in accord with diffusion kinetics (24).

Stain that is removable by a nonoxidative detergative process is of little practical concern. However, stain that resists removal by detergent has to be destroyed by an enzyme or by bleaching.

Bleaching. Oxidation with peroxygen bleaches involves three reactions: i) conversion of hydrogen peroxide to a peroxycarboxylic acid by perhydrolysis; ii) bleaching in solution of stain desorbed from the fibers; and iii) bleaching of stain located within the fibers. Perhydrolysis

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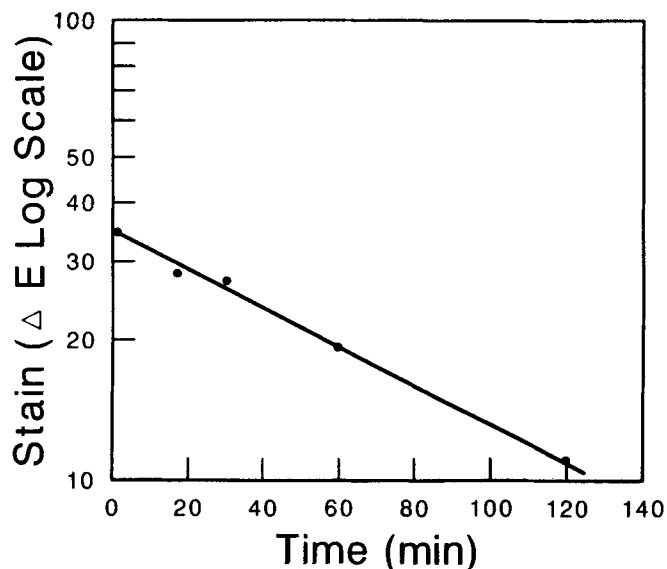


FIG. 13. Bleaching of erythrosin (FD&C Red 3) on cotton with a solution containing 0.024 M peracetic acid and 0.0056 M sodium pyrophosphate at 25°C, pH 4.0.

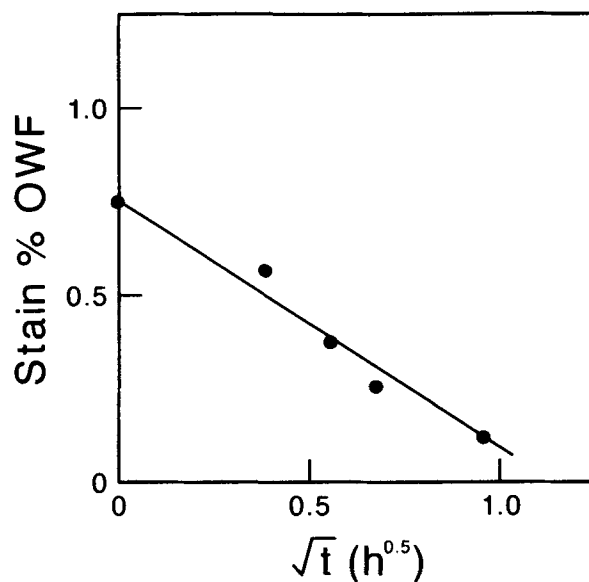


FIG. 15. Bleaching of Safranin O on cotton with peracetic acid at 25°C. Residual stain was determined by extraction with *N,N'*-dimethylformamide (DMF), containing 0.40 M zinc chloride, 8 mL/L HCl and 0.023 M 2,6-di-*t*-butyl-4-methylphenol (22).

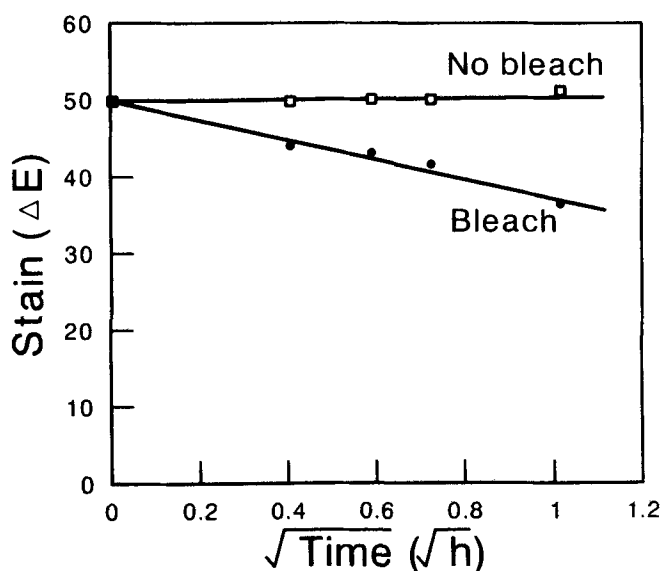


FIG. 14. Bleaching of Safranin O on cotton with a solution containing 0.029 M peracetic acid, 0.06 g/L Mersol SE and 0.005 M sodium carbonate at 25°C, pH 4.4.

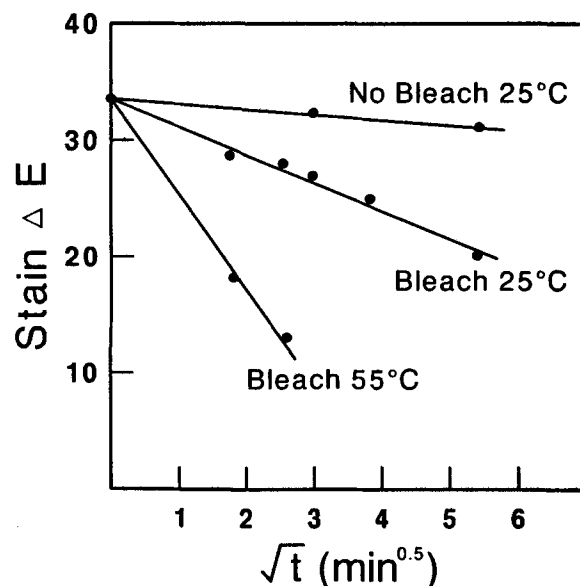


FIG. 16. Bleaching of Eriochrome Black T on nylon with a solution containing 0.025 M sodium perborate, 0.0125 M NOBS and 0.056 M sodium pyrophosphate at 25°C and 55°C. Initial pH 9.18, final pH 9.17.

and synthetic food dyes varies widely. Bleaching has to be selective, destroying the unwanted coloration but leaving the dyes proper unchanged. The relative bleaching rates shown in Figure 10 suggest that a synthetic food dye, FD&C Red 40, may be more difficult to bleach than some textile dyes, for example the C.I. Acid Blue 90. However, the relative rate at which a color is bleached in

solution does not necessarily predict the bleaching rate in fibers.

Bleaching of stain residing within fibers is much more difficult than bleaching in solution. The bleaching rate in fibers is much slower than in solution. Bleaching rates in solution do not correlate with those for bleaching in fibers (13). Hence the mechanisms must be different.

Bleaching of stain located within fibers has to occur by one of two plausible mechanisms (Fig. 11): i) The stain diffuses from fibers into the bath and is bleached there; and ii) The bleaching agent diffuses into the fibers and bleaches the stain within the fibers. It is possible that bleaching involves both mechanisms (26).

Our results indicate that the kinetic order of the bleaching process depends on the diffusion rate, the location and affinity of the stain to fibers (Fig. 12). Tea stain has no affinity to polyester fibers and is desorbed rapidly. Bleaching of tea stain on cotton involves rapid desorption of the stain from the fiber surface, followed by a slower diffusion-governed bleaching process. Tea stain has a strong affinity to nylon and is very difficult to bleach.

A colorant that has no affinity to fibers is desorbed from fibers and bleached in solution mainly by a pseudo-first-order process (Fig. 13). Bleaching of a washfast stain in fibers, such as a synthetic food color in polyamide fibers, exhibits a linear relationship between the amount of stain bleached and the square root of time (Figs. 14–16). This suggests a diffusion process. In the absence of a bleaching agent, no significant amounts of stain were removed from the fibers. The argument, that the stain diffuses into the bath and is bleached there, has the burden of explaining why the outward diffusion of the stain is greatly accelerated by the bleaching agent in the bath. It is therefore likely that bleaching of a washfast stain occurs within fibers or in the subsurface of fibers. The bleaching agent may diffuse into the fibers or into the subsurface of the stained fibers. The mechanism of bleaching within fibers is supported by the observation that activated perborate can bleach a reactive dye covalently bonded to cellulose. On the other hand, a bleaching agent sorbed in the fiber surface can destroy the stain there and cause a diffusion of the colorant from the inside of the fibers to the outer perimeter, where bleaching occurs.

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