Coffee Stain on Textiles. Mechanisms of Staining and Stain Removal[1]

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ABSTRACT: Coffee stains on textiles are mainly caused by the water-soluble and acidic colored substances in coffee. The acidic nature of coffee stain has been shown by ultraviolet and visible spectroscopy of coffee as a function of pH; ion-pair formation with a cationic surfactant and titration with Hyamine 1622 and a surfactant-specific electrode; and precipitation of the colored components in coffee with barium hydroxide as a barium salt. The permanence of coffee stains on textiles depends on the nature of the fibers. The affinity of coffee stain to fibers, indicated by resistance to detergency, increases in the order polyester < cotton < nylon. Coffee stain has little affinity to polyester fibers but adheres to cotton and even more firmly to nylon. The strong affinity to nylon and the pH dependence of staining suggest an ionic interaction of carboxyl and phenolic groups with amine end-groups in nylon. The ionic attraction is augmented by nonionic interactions that are enhanced by the oligomeric or polymeric nature of the staining substances. In accord with the dominantly acidic character of coffee stain, an alkaline medium is needed for the dislodgment of coffee stain from nylon fibers. Bleaching of coffee in solution with perborate, activated with sodium *n*-nonanoyloxybenzenesulfonate, or Oxone® (DuPont, Wilmington, DE) obeys pseudo first-order kinetics. Oxone, a peroxysulfate triple salt, is a more powerful oxidant for coffee stain than sodium perborate, but its use is limited by the bleach fastness of dyes.

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KEY WORDS: Bleaching of coffee stain, coffee color, coffee stain on textiles, mechanisms of staining, mechanisms of stain removal, oxone, sodium perborate, stain resistance of nylon.

Coffee is a popular beverage, and coffee stains on textiles are common, especially on tablecloths and on carpets. It is therefore of a substantial practical interest to understand the nature of the stain and the mechanisms of staining.

EXPERIMENTAL PROCEDURES

Materials. Cotton, polyester (Dacron Type 54), and nylon-66 yarn and fabrics were obtained from Testfabrics, Inc. (Middlesex, NJ). Cotton yarn was immersed in 5% NaOH, containing 0.01 g/L Merpol SE (DuPont, Wilmington, DE), 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-66, Type 1500 Superba heatset yarn were extracted with petroleum ether. The nylon-66 white level-loop carpet was scoured and cut into 10 × 12 cm swatches before staining.

Instant coffee, used in staining experiments, was made by dissolving 12.5 g/L Folgers Crystals (Procter & Gamble, Co., Cincinnati, OH) in hot water and cooling the solution to the temperature stated. The staining propensity of instant coffee was similar to that of brewed coffee. Sodium perborate, monohydrate, and Oxone® were from DuPont Co..

Procedures. Bleaching in solution was measured at ambient temperature (24°C) with a Hewlett-Packard diode array double-beam spectrophotometer (Model 8450A; Hewlett-Packard, Palo Alto, CA). The pH of the components was adjusted with NaOH and Na_2CO_3 before mixing.

An Ahiba Texomat, Model 1000 (Ahiba Texomat AG, Birsfelden, Switzerland), equipped with 400- or 800-mL Pyrex beakers, was used to stain or wash yarn, fabrics, and carpet (10 × 10-cm swatches). The Ahiba Texomat has the following advantages over a Launder-Ometer (Atlas Electric Devices, Co., Chicago, IL) or Terg-O-tometer (U.S. Testing Co., Inc., Hoboken, NJ): (i) the beaker is transparent, and the bleaching or detergent process can be followed visually; and (ii) possible catalysis of bleaching by metal walls of the beaker is excluded.

The color of stained yarn or fabrics was measured in the CIE L*a*b* color space with a Minolta CR-200 chromameter. The procedures for reflectance measurements of stained yarn and fabric have been described previously (1). The technique for measuring the color of stained carpet is the subject of a forthcoming paper (2). The color measurements were supported by extraction of coffee from nylon yarn. Stained nylon yarn (0.10-g sample size) was extracted repeatedly at 140°C with 10 mL portions of *N,N*-dimethylformamide that (DMF) contained 5 g/L 2,6-di-(*t*-butyl)-4-methylphenol and 50 mL ethanolamine, until the fibers were colorless. The fibers were covered in an Erlenmeyer flask with the solvent, the flask was loosely stoppered and placed into an oil bath, heated at 140°C, for 3 min. The extracts were combined, diluted to 50 mL with the extraction solvent, and the absorbance of the combined extract was measured in the spectrophotometer. The extraction

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technique and equipment have been described before (3). The absorbencies of the extracts corresponded to the color values obtained by reflectance measurements.

RESULTS AND DISCUSSION

Composition of coffee stain. Although coffee has been consumed for centuries, the chemical composition of coffee is largely unknown. Coffee is a complex mixture, and over 700 components have been detected so far. The various classes of chemical compounds found in coffee are (approximately): caffeine, 2–5%; acids, 7–17%; trigronelline, 1–2%; protein, 1–6%; sugar, 1–5%; polymeric carbohydrates, 30–50%; and colored ingredients, 20–35% (4–7).

Coffee contains a substantial amount of colored matter. The structure of colored species in coffee is not known in detail. Coffee contains brown to black pigments, polymers, and water-soluble colored substances.

Because coffee contains water-insoluble suspended particles, we examined the effect of particulate matter on staining. We compared stains made with coffee before and after removing particular matter from the brew. Filtration of coffee through a fine filter with a 0.2-micron pore size removed most of the particles but did not significantly affect the intensity of the stain. The particles in coffee have a negative zeta potential (Table 1) and are not strongly attracted to fibers because most textiles also have a negative surface potential in water. Hence, particulate matter is not a major factor in the staining process. Coffee stain is caused mainly by colored components that are molecularly or colloidally soluble in coffee.

The hydrophilic nature of the stain is evident from the solubility of colored components in solvents and from partitioning of coffee color between water and a solvent. When ground roasted coffee or instant coffee powder is extracted with anhydrous organic solvents, such as hydrocarbons, esters, ketones, ethers, chlorocarbons, etc., the extracts are either colorless or contain only a small fraction of the colored components. Instant coffee, made by extracting roasted beans with water and drying the extracts, has retained its staining propensity. Hence, the staining components of coffee are hydrophilic and soluble in water, either molecularly or colloidally.

Water-soluble stain components. According to common belief, coffee stain has the characteristics of a nonionic material that behaves like a pigment or a disperse dye, a nonionic dye without anionic or cationic functions. We have found, however, that coffee stain is caused by acidic substances.

TABLE 1
Particulate Matter in Percolated Coffee

Coffee	Particle size average (μg)	Zeta potential (mV)
Percolated coffee		
Unfiltered	201	−21.8
Filtered	134	—[a]
Instant coffee		
Unfiltered	538	−10.8
Filtered	—	—

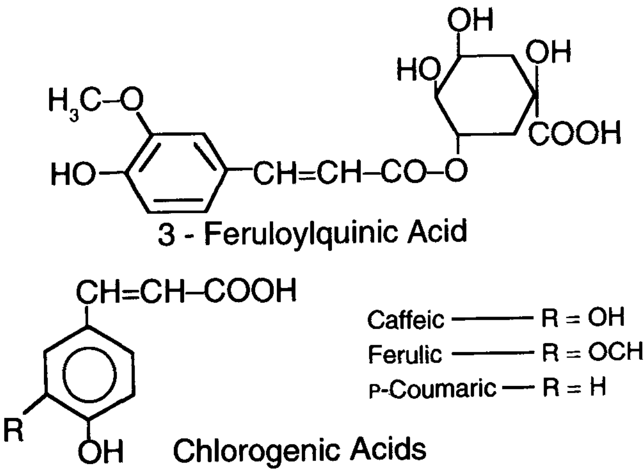
[a] Insufficient concentration of particles for measurement.

Coffee is an acidic beverage. The pH of percolated coffee is 4.9, and the pH of instant coffee made from Folgers Crystals is 5.0. Coffee is known to contain phenolic acids (4–6), mainly chlorogenic acids (7,8) (Scheme 1), smaller amounts of nicotinic acid, and aliphatic acids that originate from cellular metabolism. These acids are colorless and cannot stain fibers. However, the acids can affect staining indirectly by forming acidic colored species in coffee.

The brown color of coffee is formed when coffee beans are roasted. During roasting, several degradation, polymerization, dehydration, fragmentation, and recombination reactions occur (5). Monosaccharides and sucrose are thermally degraded and polymerized to caramel, a brown substance. The caramel can react with chlorogenic acids to form brown–black substances that resemble humic acids (5,9,10). Another reaction mechanism is the formation of melanoidins from amino acids and sugars. The precursors for the colored products are: saccharides, sucrose for caramel; amino acids for melanoidins; chlorogenic acids for humic acids.

Useful information on the nature of the staining components in coffee can be obtained by ultraviolet (UV) and visible spectroscopy. The spectra of coffee exhibit two absorption peaks in UV at 306 and 329 nm (Fig. 1). The visible brown color is the shoulder of the UV peak. When coffee is made slightly alkaline by adding 1.0 g/L sodium carbonate, the spectra shift considerably, and the color of coffee changes visibly. This color change indicates that the colored substances in coffee are acidic. Neutralization of the acidic groups, for example phenolics, produces an anion of different color.

The acidic and, consequently, anionic nature of coffee color is also supported by the formation of water-insoluble ion-pairs with a quaternary amine, such as a cationic surfactant. We titrated coffee with Hyamine 1622 by using a surfactant-specific electrode and consumed 0.85 meq of the cationic surfactant per liter of coffee.



SCHEME 1

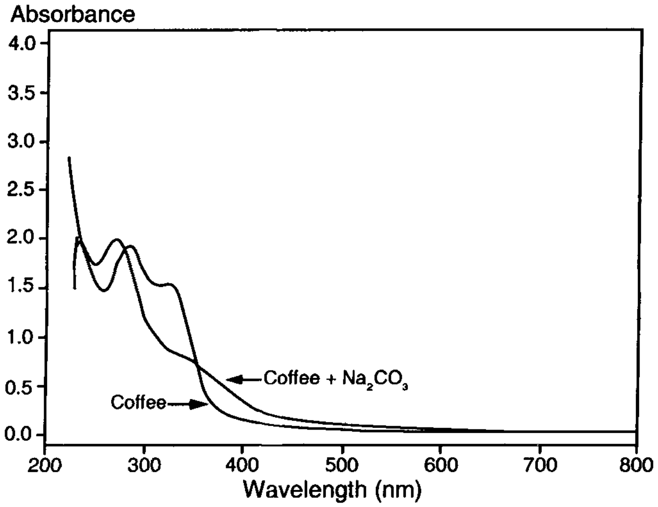


FIG. 1. Spectra of coffee. Effect of alkali (1.0 g/L Na_2CO_3) on coffee color.

Further evidence of the acidic nature of coffee color is provided by salt formation with inorganic bases. Because the barium salts of the colored substances in coffee are only slightly soluble, barium hydroxide precipitates about 80% of the colored matter in coffee. The filtrate of the precipitated components is a weaker stain, even after being acidified to the initial coffee pH value. This result indicates that staining with coffee is dominated by colored substances with an acidic function.

Staining. In the absence of a stain-resist finish, sorption of the colored species of coffee by nylon is initially rapid, followed by a slow diffusion that leads to saturation (Fig. 2). A curve of essentially the same shape is obtained by extracting the sorbed coffee stain quantitatively from fibers and plotting the absorbances of the extracts instead of ΔE values. The diffusion of coffee into nylon fibers is greatly accelerated by heat (Fig. 3). Because coffee is usually consumed hot, spilled coffee is a real challenge to stain prevention.

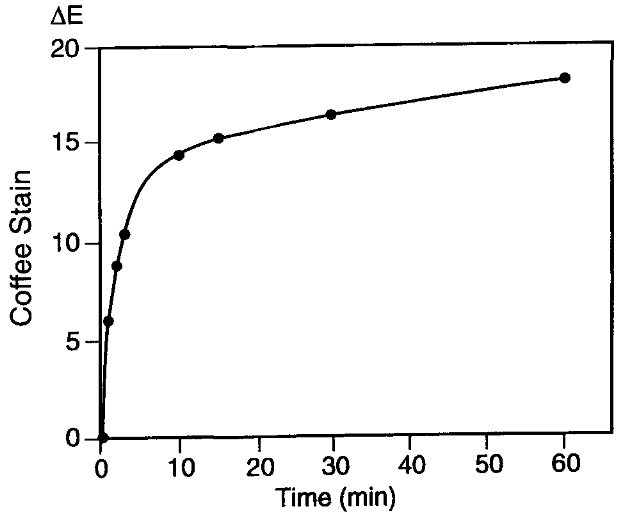


FIG. 2. Staining of nylon-66 carpet with coffee at 25°C as a function of time.

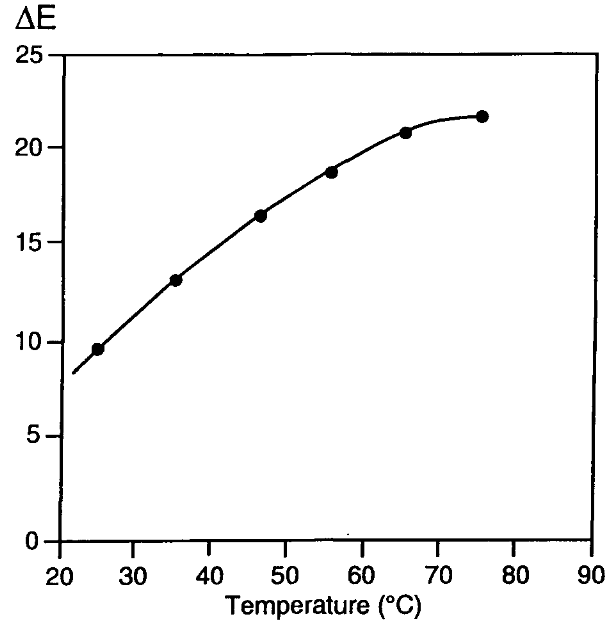


FIG. 3. Effect of coffee temperature on staining of nylon-66 carpet (5-min immersions).

The concept that the staining components of coffee are soluble in water raises the question: Why are coffee stains on fabrics difficult to remove by washing? The answer to this question is the affinity of coffee stain to fibers. This interaction between coffee and fibers depends on the nature of the fibers. Coffee discolors most fibers when allowed to dry on the fibers. However, a coffee stain can be readily removed with an aqueous detergent from some fibers but not from others.

We immersed polyester, cotton, and nylon yarn in coffee, rinsed the yarn with water and allowed the yarn to dry. Coffee had stained all the yarns to some extent (Table 2). However, the resistance of coffee stain to removal with an aqueous detergent revealed great differences in the affinity of the stain to the fibers. The affinity of coffee stain to fibers increases in the order: polyester < cotton < nylon. Washing for 10 min with 2.0 g/L Tide (no bleach) at 25°C removed essentially all of the stain from polyester, a substantial amount of stain from cotton, but very little from nylon (Table 2).

The strong affinity of coffee stain to nylon fibers provides useful information on the nature of the coffee stain. Staining

TABLE 2
Coffee Stain on Yarn

	Coffee stain (ΔE)	
Yarn	Before washing	After washing
Polyester[a]	17.4	0.9
Cotton	19.6	12.5
Nylon-66	25.0	23.5

[a] Dacron T54. All fabrics from Testfabrics, Inc. (Middlesex, NJ).

of nylon with coffee depends on the acidity of coffee. When coffee is made alkaline, sorption of coffee stain on nylon decreases with increasing pH (Fig. 4). The pH dependence of staining suggests an ionic interaction between the carboxyl groups of the staining components and the amine end-groups of nylon. Hence, staining with coffee resembles dyeing of nylon with an acid dye. It is well known that acid dyes are sorbed onto nylon in an acid medium and that the dye sorption decreases with increasing pH (11). In an acid medium, the amine end-groups in nylon are protonated and form a cationic site for the anionic dye (12). Coffee stains nylon in a similar fashion, albeit with some significant differences.

Unlike acid dyes, the colored substances in coffee are oligomeric or polymeric, formed by thermal degradation and condensation reactions. The higher-molecular weight species can have several attachment points to the fibers. Most colored compounds in coffee feature hydroxyl groups that can form hydrogen bonds with fibers. Aromatic groups and conjugated systems can increase the attraction to fibers by molecular (Van der Waals or dispersion) forces. Although these nonionic bonds are weaker than an ionic bond formed between an amine end-group and an acid, the multitude of nonionic bonds can make a considerable contribution to affinity and hinder stain removal.

Stain removal. The desorption of coffee stain from nylon fibers is dominated by the acidic character of the stain. Water does not extract coffee stain from nylon fibers, unless the water is made alkaline (Fig. 5). Alkali converts carboxylic and phenolic groups to the corresponding salts that have little affinity to nylon. Hydrogen bonds formed between the hydroxyl groups of the colored species and the fibers are broken by alkali as well.

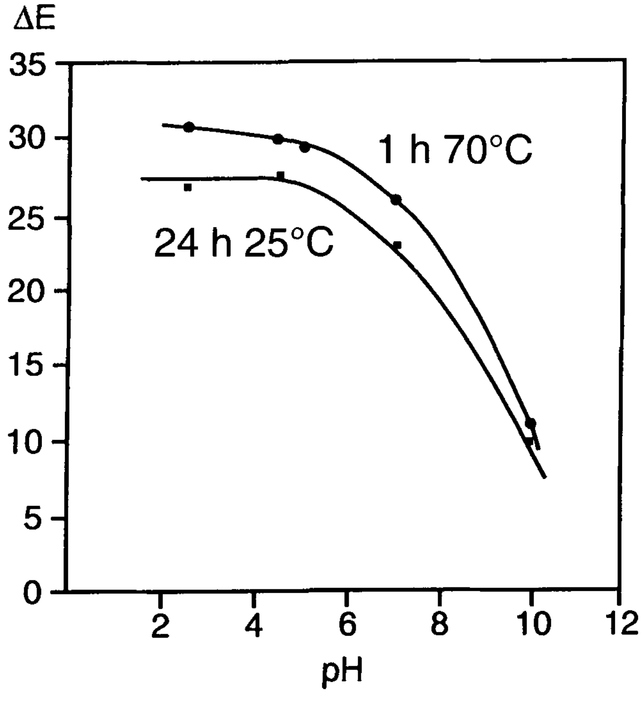


FIG. 4. The pH dependence of staining nylon-66 with coffee.

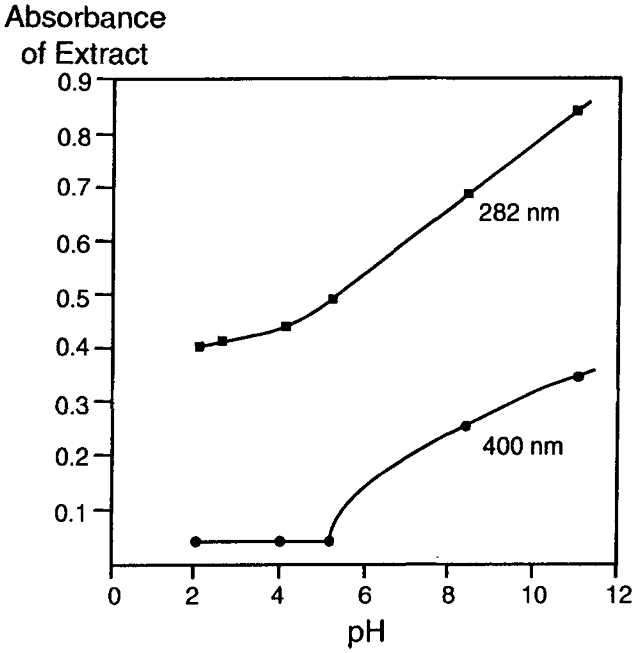


FIG. 5. The effect of pH on the color of water extracts from coffee-stained nylon-66 carpet, extracted with various buffers at 25°C.

An aqueous solution of sodium carbonate or sodium hydroxide does not extract coffee stain from nylon completely. Coffee stain can be removed quantitatively from nylon with hot DMF that contains ethanolamine. Unfortunately, this solvent will also extract the dyes from the carpet yarn. Hence, this extraction procedure is useful for analytical purposes only.

Bleaching. Because coffee stains are difficult to remove from nylon by washing or shampooing with a detergent alone, the stain may have to be bleached. The bleaching reaction with sodium perborate activated with sodium *n*-nonanoyloxybenzenesulfonate, or Oxone obeys pseudo first-order kinetics in solution (Fig. 6). The bleaching rate of coffee with sodium perborate activated with sodium *n*-nonanoyloxybenzenesulfonate is relatively slow at ambient temperature. Oxone, a peroxysulfate triple salt, is a much more powerful oxidant for coffee than is sodium perborate activated with sodium *n*-nonanoyloxybenzenesulfonate. However, it is not feasible, at least not now, to formulate a laundry detergent with peroxysulfate. To use Oxone as a spot remover is feasible, but is limited by the bleach fastness of dyes. This limitation leads to the fundamental principle that governs bleaching processes. A bleaching process is successful when the bleach fastness of the stain and that of the dye in fibers are wide apart. If the bleach fastnesses are close, bleaching of the stain is not possible without damaging the dye. Hence, the higher the bleach fastness of the dyes in the fibers, the broader the spectrum of bleaching agents available for the removal of coffee stains.

Principally, there are three solutions for eliminating coffee stains: (i) use dyes or pigments that are much more bleach-fast than coffee and allow the use of strong bleaching agents;

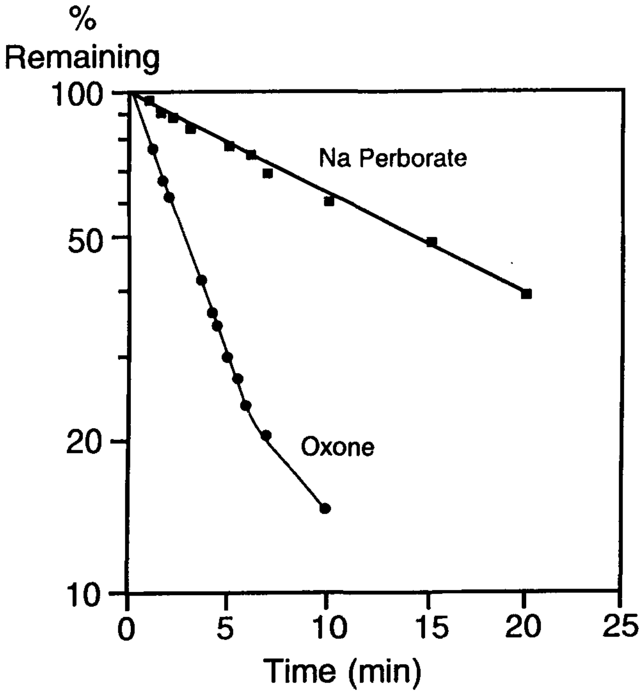


FIG. 6. Bleaching of coffee (0.50 g/L instant coffee) at 25°C with (■) 2.5 g/L of sodium perborate, monohydrate [0.38 g/L active oxygen (AO)] activated with 1.25 g/L sodium *n*-nonanoyloxybenzenesulfonate; and (●) with 5.0 g/L Oxone® (DuPont, Wilmington, DE) (0.23 g/L AO). The pH of the components was adjusted to 9.0 with NaOH and Na_2CO_3 before mixing the components.

(ii) use a stain-specific cleaning agent, such as an enzyme, that does not affect the fibers and dyes in the fibers; and (iii) provide the fibers with a finish that resists staining by hot coffee. The obvious solution, to avoid spilling coffee on tablecloths and carpets, is not realistic.

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