

The Kinetics of Dye Rinse from Bleached Hair

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Synopsis—Experimental data were obtained on the KINETICS of DYE RINSE from BLEACHED HAIR. It was found that dyes of different molecular sizes had significantly different behavior towards the effect of hair bleaching.

INTRODUCTION

There is still considerable uncertainty regarding the chemistry of hair bleaching; however, it is generally agreed that oxidative bleaching has several side effects (1-3): changing the chemical constituents of the hair, opening the highly crosslinked structure inside the hair fiber, and possibly degrading the cuticle layer on the surface. These modifications conceivably alter the dyeing properties (4, 5) of hair, in particular the kinetics of dye rinse. Aside from the obvious practical implication, results on the kinetics of dye rinse from bleached hair can be of considerable theoretical interest, at least qualitatively.

This study has been limited to rinse-out kinetics of direct dyes. However, the ionic character and molecular sizes of the dyes have been considered.

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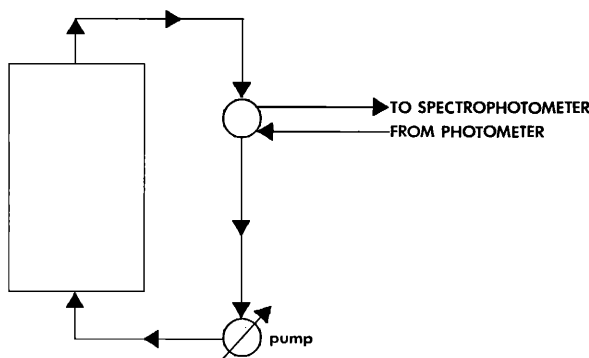


Figure 1. Schematic of rinse-out apparatus

EXPERIMENTAL

Figure 1 is a schematic showing the continuous measurement of dye concentration as the dyed hair is being rinsed. The rinsing was done inside a rectangular box made of transparent plexiglass. One side of the box could be detached for inserting and changing samples. Inside the rinsing box the hair sample was confined in a rectangular cage.

One part of the cage was made from a thin slide of plastic with a hole cut in the middle. A piece of $1/16$ in. wire screen was mounted on the bottom of the hole. When the hair sample was in place, a second similarly constructed piece was put on top of it as a cover, and secured to it by a set of screws. The cage was then slid into the box between two slots. In each run of the experiment, four such cages were usually used for 1 g of hair sample.

With the help of a liquid pump, water was circulated through a cell in a spectrophotometer* where the dye concentration was continuously recorded. The rinsing of dyed hair was done at room temperature.

Bleached hair was obtained by treating normal brown hair with a commercial hair bleach.† The bleached hair was rinsed with water for 2 hours to leach out any residual persulfate. The bleached sample was then dyed‡ to equilibrium. The concentration of the dye bath was 1 g/liter. The residual dyes on the surface of the hair were removed by leaving the dyed sample in a centrifuge§ at 10,000 rpm for 45 min.

* Gilford 2000, Beckman Instruments, Inc., Fullerton, Calif.

† Ultra Blue, Clairol Inc., Stamford, Conn.

‡ Dyes were prepared at Clairol Research Lab. except Acid Green 25 and Deorlene Orange, which were obtained from Ciba Chemical and Dye Co., Fair Lawn, N. J.

§ International Centrifuge, Model HG, International Equipment Co., Needham Heights, Mass.

RESULTS AND DISCUSSION

Some studies have been published (6-9) showing the effect of molecular geometry on the dyeing kinetics of fibers. One aspect of this effect is amply demonstrated by the results shown in Figs. 2, 3, and 4, especially the difference in behavior between large and small molecules towards the degree of bleaching. In these graphs, $T_{1/2}$ is plotted against the amount of bleaching the dyed hair previously received, where $T_{1/2}$ is the time for half of the dye to be rinsed out of the dyed sample. A decrease in $T_{1/2}$ would indicate an increase in rinse rate. It can be seen from these graphs that small molecules show a continuous decrease in $T_{1/2}$, while in the case of relatively larger molecules, $T_{1/2}$ actually increases until it reaches a peak. This increase in $T_{1/2}$ seems to indicate that, as a result of oxidative bleaching, the dye-substrate interaction becomes stronger, since the molecular diffusion rate within the fiber would only increase with the amount of bleaching.

To explain the above phenomenon, it is convenient to introduce a concept that involves both the binding-site availability and chemical

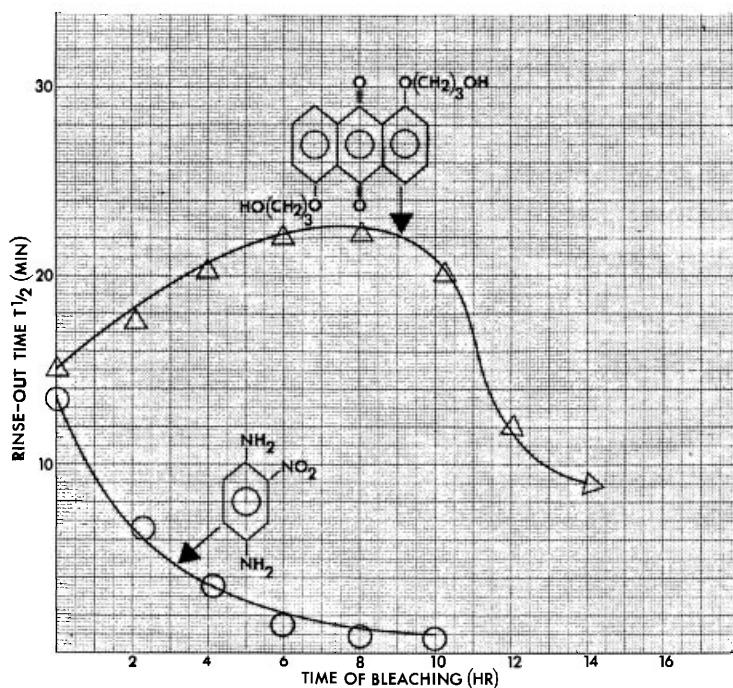


Figure 2. Kinetics of rinse-out of neutral dyes

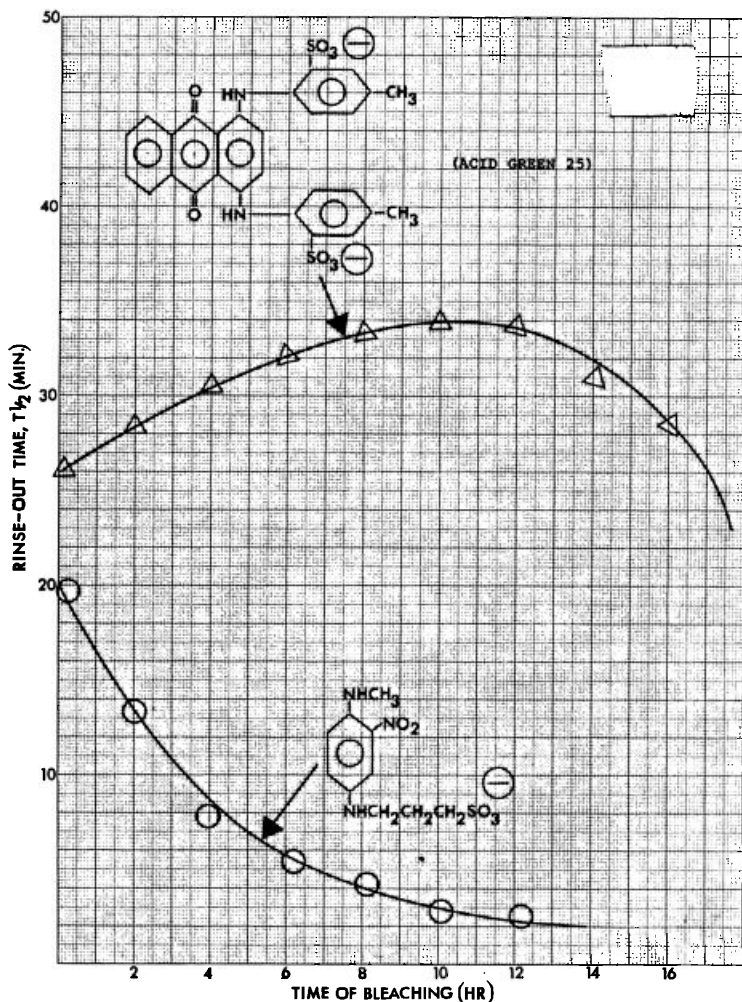


Figure 3. Kinetics of rinse-out of anionic dyes

affinity between dye molecules and substrate. A binding site is referred to as any location inside the hair to which a dye molecule would attach.

Since the internal structure of unbleached hair is highly crosslinked, it can be expected that the movement and penetration of large molecules inside the fiber are limited. But when the hair structure becomes a bit more open as a result of being bleached, this large molecule would be able to reach into some otherwise hindered positions. In other words, there is an increase in available binding sites. Since the hair samples were dyed to equilibrium, the rate at which the dye molecule gets into

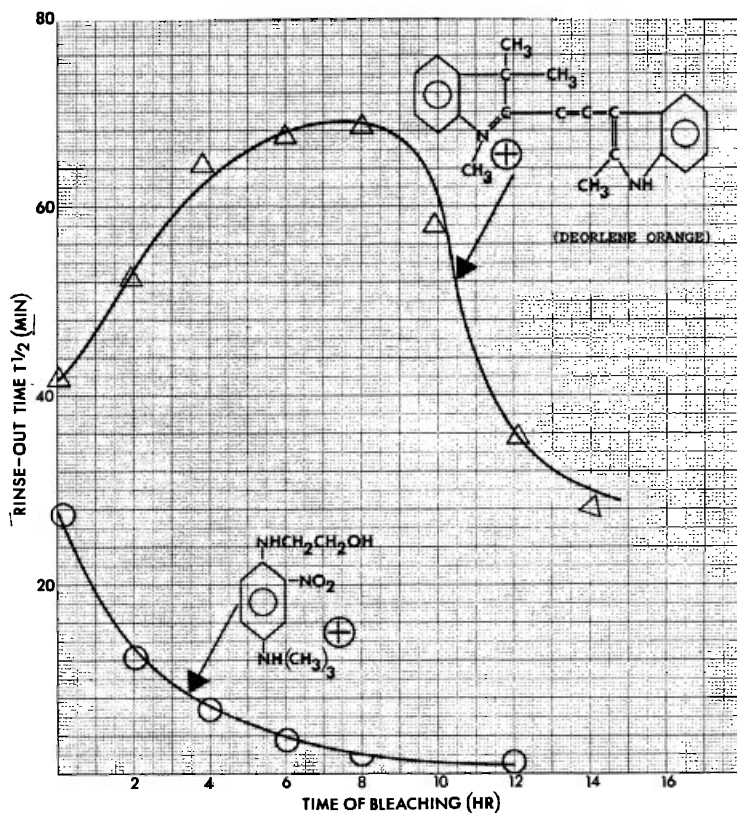


Figure 4. Kinetics of rinse-out of cationic dyes

the sites is of no consequence. However, once they fall into these sites, they stay there as if they were trapped, either due to some steric constraints surrounding them, or due to an increase in chemical affinity. The increase in affinity can be a result of larger contact area between dye molecules and substrate, or, to a lesser degree, a modification of the chemical nature of the substrate, thus contributing a stronger interactive force between them. As long as the increase in site availability and affinity is large compared to the increase in molecular diffusion, the overall rate of dye rinse from bleached hair would slow down with the amount of bleaching. This behavior would continue until the molecular size is comparable to the internal "holes" of the bleached hair fiber so that site availability is no longer a factor. Because of the very open structure within the fiber and possibly the increasing damage to the cuticle layer, the diffusion rate would predominate; therefore, when bleaching reaches a critical stage, the rate of dye rinse starts to increase.

However, the movement of small molecules is much less restricted inside the hair fiber, and a gradual opening of internal structure affects site availability little. Chemical modification of the hair could bring about a stronger interactive force between dye and substrate (as it does to large molecules). This effect might not be large enough to compensate for the corresponding increase in molecular diffusion inside the fiber as a result of bleaching. It seems that at practically any degree of bleaching, the kinetics of dye rinse are diffusion-controlled for small dye molecules.

Even though neutral and ionic molecules behave similarly towards the effect of bleaching, the $T_{1/2}$ values are generally higher for ionic dyes. It seems that electrostatic force plays only a secondary role in determining the kinetics of dye rinse from bleached human hair. However, more extensive data are necessary to establish this conclusion.

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