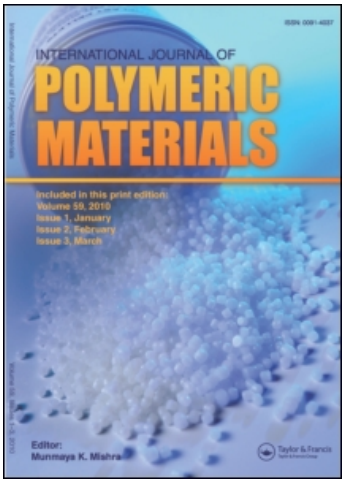

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The Importance of the Diffusive Transfer of Tints in the Technology of Tinting of Soft Contact Lenses

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This paper deals with the kinetics of tint transfer in soft contact lenses. A mathematical model taking into account both diffusion and chemical reactions is proposed and physicochemical parameters are determined. It is shown that bulk tinting is more effective in practice than surface tinting.

KEY WORDS dyeing, soft lenses, polymers

Issues relating to the use of soft contact lenses (SCL) have recently been widely discussed,[1–4] but we feel the interaction of SCL with active tints has been neglected.

Experience with SCL of various colors has demonstrated that they can provide a reliable cosmetic effect and, simultaneously, visual correction in patients with a partial transparence in the central corneal zone. Even in aphakic patients and also those with iris defects.[5]

The major problems consist of finding appropriate tints, elaborating a technology for tinting cosmetic contact lenses (CCL), meeting the requirements of biological inertness, and in obtaining reproducible, stable colors and tints (tints must not change during the process of sterilization or storage in distilled water or other media). To solve these problems, information is needed on the interactions within the polymer-tint system. It is noteworthy that traditional empirical methods of selecting tints and tinting techniques[5,6] provide for only a limited effect.

The purpose of our research is to study the kinetics of the transfer of tints within SCLs and to formulate recommendations on changing the technology of lens tinting so that the above requirements can be met.

MATERIALS AND METHODS

SCLs manufactured from poly(2-hydroxyethylmethacrylate) (water content = 38%) are tinted. Plano, equal-thickness (thickness = 0.1 mm) lenses are used. Alcoholic

solutions of tints (blue, gray and brown) manufactured by Titmus Eurocon Kontaktlinsen are used as the tinting material.

Lenses were tinted at the All-Union Research Institute for Eye Diseases using the techniques of surface and bulk tinting.

The quantity of a tint desorbed from lenses during their contact with the aqueous solution is spectrophotometrically registered in the visual and ultraviolet (uv) ranges by DU-65 Beckman instruments. The relationship between the optical density of tinting solutions and their concentrations, as compared with the initial concentration (for all tints), satisfies the Beer–Lambert law

$$A = \varepsilon \frac{C}{C_0}$$

where ε is the actual extinction (dish thickness is constant, $1 = 1$ cm), A is the optical density, C is the concentration of tint in the solution, and C_0 is the initial concentration of tint.

Desorption of a tint from lenses is studied under conditions of contact between the polymer and the saline solution simulating the lacrimal liquid. Desorption of a tint is also studied during thermal sterilization. Desorption experiments allow a comparative analysis of the rate of liberation of tints and their degree of fixation in lenses.

RESULTS AND DISCUSSION

Figure 1 shows kinetic curves depicting the desorption of tints from SCLs at room temperature (i.e., under the conditions of lens storage). It appears that there are two forms of tint in the polymer, i.e., free material (easily librated from the matrix) and fixed material (the concentration in a lens does not change with time under isothermal conditions). The process of fixing a tint in lenses can be represented as a reversible reaction:

$$B_f + \ominus \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B_a \qquad (1)$$

where B_f is a molecule of the diffusing tint, $\ominus$ is the center of interaction "tint-polymer," B_a is a fixed molecule of a tint, and k_1, k_{-1} are rate constants.

At room temperature (23°C), the equilibrium is strongly shifted toward the fixed form and reaction (1) becomes virtually irreversible. The transfer of a tint within the polymer occurs according to the following equation:

$$\frac{\partial C_f}{\partial t} = D \frac{\partial^2 C_f}{\partial x^2} - k_1(C_\infty - C_a) \cdot C_f + k_{-1} C_a \qquad (2)$$

where C_{f1} and C_a are the concentration of the free and fixed forms of tint, D is

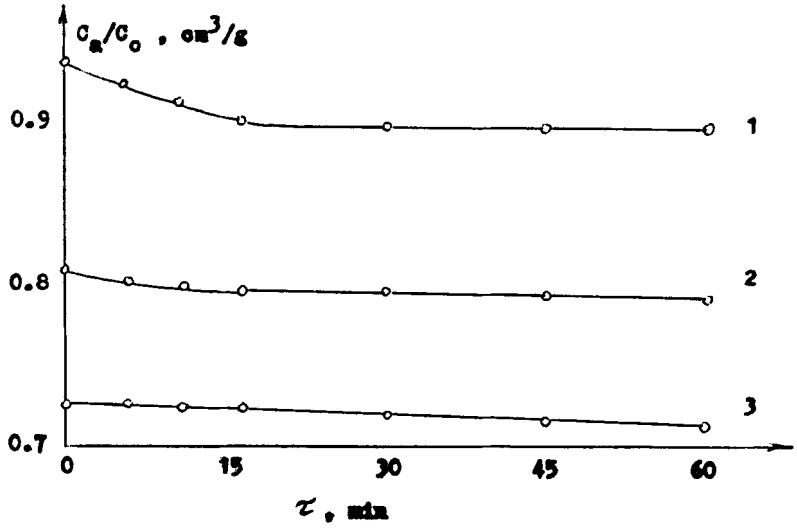

FIGURE 1 The kinetics of desorption of the free form of a tint from lenses. (1) Blue. (2) Brown. (3) Gray.

TABLE I

Parameters of sorption and diffusion of tints in SCLs

Tint	C_a/C_0 cm³/g	C_f/C_0 cm³/g	$D \cdot 10^8$ cm³/sec
Blue	0.88	0.05	1.9
Brown	0.78	0.02	0.5
Gray	0.71	0.01	0.6

the diffusion constant of the free form, C_∞ is the initial concentration of interaction centers.

For an irreversible reaction, equation (2) can be written as follows:

$$\frac{\partial C_f}{\partial t} = D\frac{\partial^2 C_f}{\partial x^2} - k_1(C_\infty - C_a)C_f \tag{3}$$

Examination of equation (3) shows that the critical concentration of the fixed form is proportional to the number of centers involved in the interaction "tint-polymer."

Table I shows relative concentrations of the fixed forms of the investigated tints (in the polymer) and the diffusion coefficients of the free forms. The largest value of C_a/C_0 is found for the blue tint; its free form has the highest diffusive mobility and, consequently, the highest rate of desorption from lenses.

As the temperature rises, the equilibrium reaction (1) shifts toward the free form which, under desorption-experimental conditions, is expected to result in complete decoloration of the lenses. This effect was observed during an experiment simulating the sterilization of lenses in a water bath at 100°C in compliance with the general

technique.[8] The desorption kinetics of tints during sterilization are shown in Figure 2. The complicated nature of the kinetic relationship is caused (apart from the diffusive stage) by the transfer of a tint from the fixed to the free form. At the beginning of desorption, this reaction can be regarded as the final stage of the process of liberation of a tint; by using an analysis of the kinetic curve, we can find its rate constant k_1. The parameters of transfer of tints during sterilization are shown in Table II. It appears that the desorption rate of tints at the sterilization temperature is similar to the sequence found for the same process at room temperature.

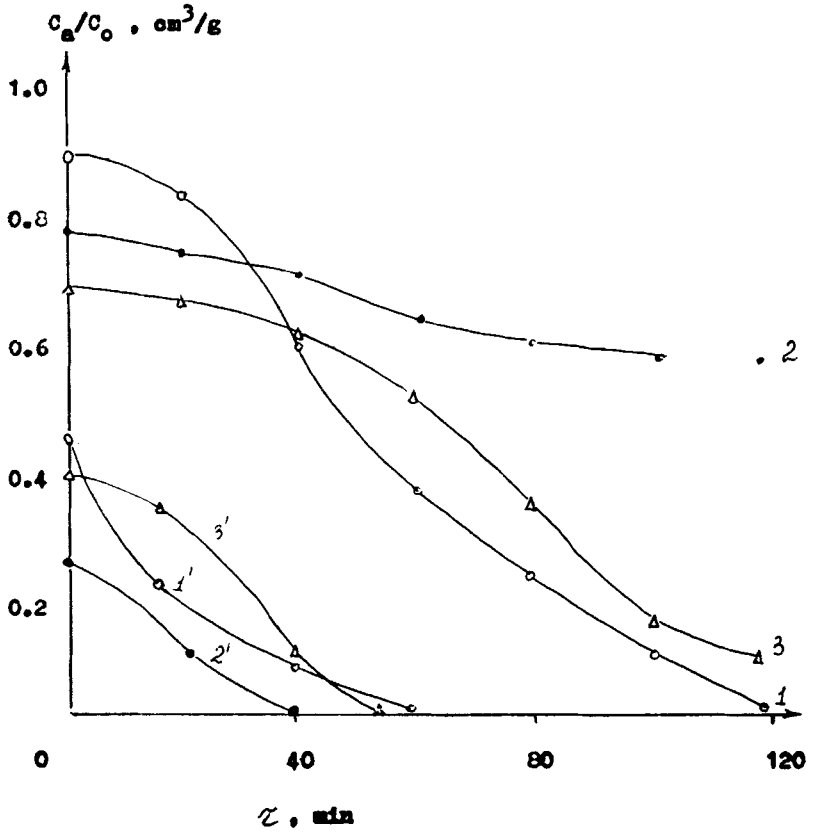

FIGURE 2 The kinetics of desorption of tints during thermal sterilization after bulk (1)–(3) and surface (1')–(3') tinting. (1.1') Brown. (2.2') Blue. (3.3') Gray.

TABLE II

Kinetic and diffusive parameters of transfer of tints in lenses during sterilization

Tint	$k_{-1} \cdot 10^5$ sec^{-1}	$D \cdot 10^8$ cm^2/sec
Blue	4	6
Brown	0.8	3
Gray	1	3

TABLE III

Relationship between the fixed and the free forms of a tint for bulk and surface tinting (C_a/C_f)

Tint	Bulk	Surface
Blue	17	2.0
Brown	39	1.7
Gray	7.1	2.5

Figure 2 and Table III show comparative data on the rate of liberation of tints from lenses tinted by the bulk and surface techniques. It is apparent that the bulk tinting technique achieves higher concentrations of the fixed form of a tint and a lower rate of desorption as compared with the surface tinting technique. This fact can be easily explained by the proposed scheme of the process.

When the surface tinting techniques is used, only those centers are involved in the reaction "tint-polymer" which are located in the subsurface layer. Thus, provided the intensities of tinting are equal, i.e., equal to total concentration of a tint in the lens, the proportion of the fixed form is expected to be larger for the bulk tinting technique, for which the effective rate of liberation is consequently lower.

Considering these factors, it can be stated that the bulk tinting technique is the most effective tinting method for satisfying the requirements, viz., reproduction of a color in manufacturing cosmetic SCLs and its guaranteed stability in storage. The data for the kinetics of transfer of tints in lenses and the estimated parameters of such transfer make it possible to predict the time for which the required SCL color will remain stable under the conditions of use with respect to sterilization time.

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