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The Effect of the Distribution of Colorant on the Color of Fibers

GEORGE GOLDFINGER, KWOK CHING LAU, and RALPH MCGREGOR, *School of Textiles, North Carolina State University at Raleigh, Raleigh, North Carolina*

Synopsis

The relationship between the color of a dyed fabric and the concentration of the dye in the system as given by the widely used Kubelka and Munk treatment is not satisfactory. A treatment by Allen and Goldfinger based on a model more appropriate for a textile substrate permits a wide variety of pertinent predictions. One of them is the calculation of the effect of a ring distribution of dye in the fiber on the color of the fabric. An experimental study of this effect is presented as supporting evidence of the validity of the Allen and Goldfinger approach.

INTRODUCTION

This experimental investigation was undertaken to test Allen and Goldfinger's theory[1] of the color of textile materials. The phenomenon of ring-dyeing provides a very sensitive test.[2,3] In the wavelength ranges in which no light absorption occurs, the distribution of the (nonabsorbing) dye obviously has no effect on the color of the sample. Similarly, the dye distribution has no effect on the color of the sample in the wavelength ranges in which one observes total absorption for both the ringdyed and the uniformly dyed samples. The ratio of the reflectance of the ringdyed sample to that of the uniformly dyed sample, R_r/R_h, is unity in these wavelength ranges.

It is known experimentally that under conditions of intermediate reflection, ringdyed samples reflect more light than homogeneously dyed samples: the ratio R_r/R_h is then greater than one. The location of the maximum value of R_r/R_h with respect to R_h provides a sensitive test of the theory. (It is frequently reported that a ringdyed sample reflects more light, behaving like a homogeneously dyed sample containing less dye. Garrett and Peters[4] proposed the first theoretical treatment of the color of ringdyed samples and correctly predicted higher reflectances for ringdyed samples than for homogeneously dyed samples. Nonetheless, statements to the contrary appear all too frequently even in the recent literature, see, for example, reference 5, page 219.)

The theoretical model describes the behavior of a parallel array of cylindrical fibers. In order to realize this arrangement and to be able to control

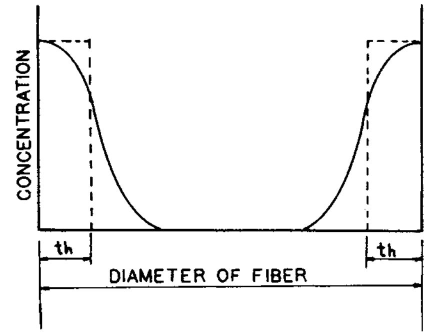

Fig. 1. Dye distribution of a ringdyed fiber: (——) real dye distribution profile; (- - - - -) idealized step distribution.

the relative ring thickness (especially with thin rings) with a reasonable dyeing time, large-diameter monofilaments with circular cross sections were necessary, and so nylon 66 monofilament of 0.22-mm diameter was used.

In the model there is a sharp boundary between the dyed and undyed portions of the fiber (Fig. 1), the concentration decreasing stepwise to zero at the boundary. This dye distribution cannot be attained in practice, but a profile close to the idealized one can be achieved by dyeing with acid dyes at high concentration and low pH. The radial concentration profile is sigmoidal,[6] as in Figure 1.

EXPERIMENTAL

Materials. "Vylor" nylon 66 monofilament, Type 0200 SA, 330 denier (0.22-mm diameter) was used. The acid dyes were Azo Phloxine G A Ex. conc. (C. I. Acid Red 1, C. I. Number 18050) and Fast Wool Blue R conc. 120% (C. I. Acid Blue 92, C. I. Number 13390).

Arrangement of Filament for Wet Processes. In order to achieve uniform treatment during wet processes, the filament was wound onto a stainless steel frame under a tension of 16.5 g. The filaments were made parallel by hand and covered the whole area of the frame ($1^1/_2$ in. × 8 in.), with 170 to 175 filaments on either side of the frame. Each frame held 77 yards of filament. In all wet processes, six such frames were arranged around a central shaft, with the filaments parallel to the shaft. The assembly rotated at a suitable speed in the appropriate liquids.

Pretreatments. Finishing additives were removed by overnight solvent extraction in carbon tetrachloride, followed by overnight rinsing in continuously replenished distilled water. The filaments were then scoured for 2 hr at 92°–95°C in aqueous sodium carbonate (1 g/l.) containing 0.05 g/l. Triton X-100, followed by thorough rinsing in distilled water.

Dyeing and Dye Redistribution. The samples were pretreated for 1 hr at 92°–95°C in aqueous formic acid (0.28 g/l.; pH 3.2) containing 0.05 g/l. Triton X-100. Sufficient stock dye solution (4.5 g/l. dye) was then added to give a final dye concentration of 1 g/l. The agitation was vigorous enough to ensure a rapid and uniform distribution of dye throughout the bath and to ensure that rate processes in the bath had no effect on the dyeing process. Dyeing was carried out for periods ranging from 10 min to several hours, depending on the depth of dye penetration desired, and was followed by vigorous overnight rinsing in continuously replenished cold, distilled water. In order to redistribute the dye uniformly throughout the filament cross section, half of the ringdyed samples were stored in formic acid solution of pH 3.2 for about 50 hr at 92°–95°C.

Estimation of Color Loss During the Redistribution Process

Due to the necessarily prolonged treatment in the formic acid solution, a color change might have arisen from causes other than the redistribution of colorant in the fiber. The magnitude of these effects was determined by colorimetric analysis.

Equal weights of corresponding ringdyed and redistributed samples were dissolved in equal amounts of formic acid to prepare three duplicate pairs of solutions. The transmittance of each solution was measured over the wavelength range of 380 to 700 nm. The ratio of the negative logarithms of the transmittance values of a given solution pair is equal to the ratio of the color concentrations of the corresponding sample pair. The average of three determinations of this ratio was used as a measure of the color loss over the wavelength range 380 to 700 nm.

The color change ranged from 5% to 50% over the wavelength range, indicating that changes other than a simple loss of dye had occurred.

The essential effects of ringdyeing were, however, apparent regardless of whether a wavelength-by-wavelength concentration correction was applied or whether the corrections were based only on the transmittance minima for the solutions.

Estimation of Ring Thickness

The filaments were embedded in a Dow epoxy resin, mixing 75% resin 332 ("hard" component) and 25% resin 732 ("soft" component) (suggested by J. H. Saunders, Dow-Badische, Williamsburg, Va.). Nine parts of this mixture were further mixed with one part diethylenetetramine, the curing agent, and stirred before pouring into the mold. The embedded sample was allowed to stand overnight. Sections were made on a sledge-type microtome at a setting of 25 microns. The optical density distributions across the sections (Fig. 2) were measured on a Joyce Loebl microdensitometer at a lever arm ratio of 1 to 500. The diameter of the filament on the recording was 11.0 cm. In order to ensure that each section was of uniform thickness, standard samples were placed in positions adjacent to the section to be measured, and all of them had to show the same optical density within +4% before the results were accepted.

The refractive index of the embedding medium was different from that of the fiber, and so a Becke line effect resulted in a loss of information at the fiber boundary. Some samples were mechanically removed from the em-

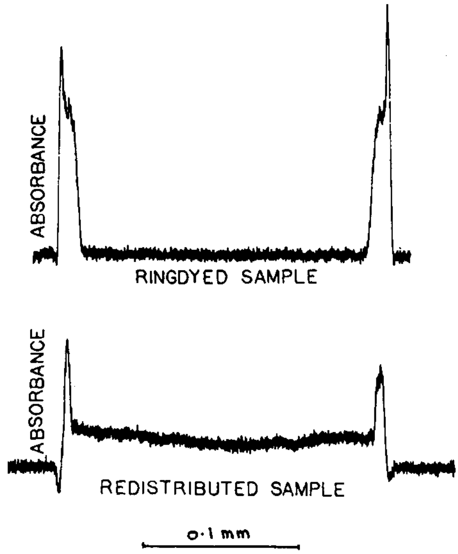

Fig. 2. Microdensitometer tracing across the diameter of a fiber cross section.

bedding medium and examined in an oil of equal refractive index, but the Becke line effect was not completely eliminated.

To determine whether this was due to incomplete removal of the embedding medium, filaments were sectioned using a sledge-type microtome with a freezing attachment, thus replacing the embedding resin with ice. The filament was wetted with distilled water and held vertically with one end in a drop of water on the freezing stage. The drop was frozen with short bursts of CO_2. More water was added, and the filament was frozen until a block of ice surrounded it. The microtome blade was cooled with Freon 22, and sections were cut at a 12-micron setting and transferred to a clean microscope slide. After air drying, the sections were mounted in an immersion oil of refractive index 1.53. In most cases, the Becke line effects were eliminated in the subsequent microdensitometry.

Presentation of the Sample for the Reflectance Measurement

In order to conform to the geometric requirements of the model, the fibers were cut into $1^1/_2$-in. lengths and packed parallel into a box molded from low-melting nylon, on a 2 in. × 2 in. glass plate. The fibers formed a flat bundle of such thickness that changes in the reflectance of the background caused no detectable difference in the reflectance of the bundle.

The use of a standard white reference gave reflectance values which included the color of the fiber itself; whereas with undyed fiber (having the same history of treatment) as the reference standard, the reflectances indicated the color due only to the colorant. When undyed fiber was boiled in formic acid solution (pH 3.2), as in the redistribution process, yellowing

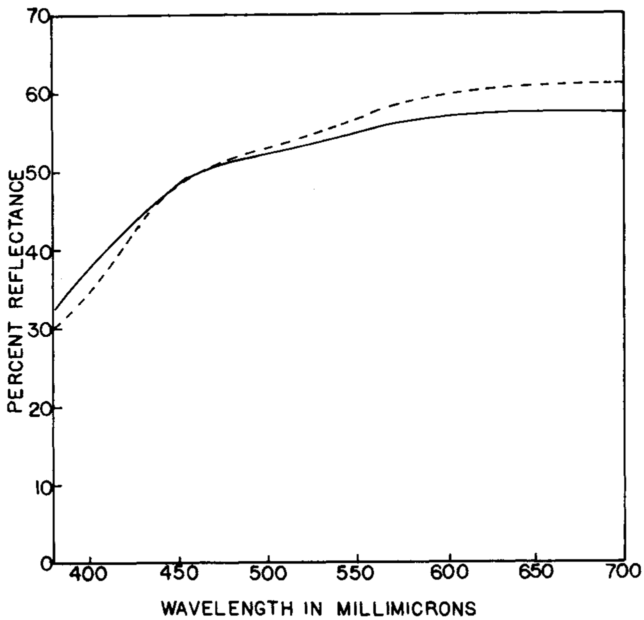

Fig. 3. Reflectance of undyed fibers: (——) treated in formic acid solution, pH 3.2, at 95°C for 1 hr; (- - - - -) treated in formic acid solution, pH 3.2, at 95°C for 50 hr.

occurred (Fig. 3). This phenomenon may also occur with dyed samples, and so the use of undyed fiber as a reference standard probably gives a better comparison between the ringdyed and redistributed samples; the yellowing effects will tend to cancel out.

Correction for the Effect of the Glass Plate on the Reflectance Value

The reflectance of the sample was by necessity measured behind a glass plate. The sample was separated from the opening of the integrating sphere by the plate, so that part of the light reflected by the sample did not reenter the sphere. The glass plate contributed some reflection of its own, which was included in the measured reflectance.

The effect of the multiple reflections of the glass plate can be readily calculated (such a calculation is given in a recent text,[5] page 302). The calculation of the light loss outside of the integrating sphere is not feasible since it depends on too many accidental factors.

It was therefore decided to carry out the correction empirically. The same sample was measured, with different numbers of glass plates in front of it. The reflectances were graphically extrapolated to zero number of glass plates (Fig. 4). As was expected, the measured reflectance was higher than the extrapolated value at low reflectance values where the contribution of the glass plate dominates. At high reflectance values, the opposite was the case, the trapping of some radiation dominating.

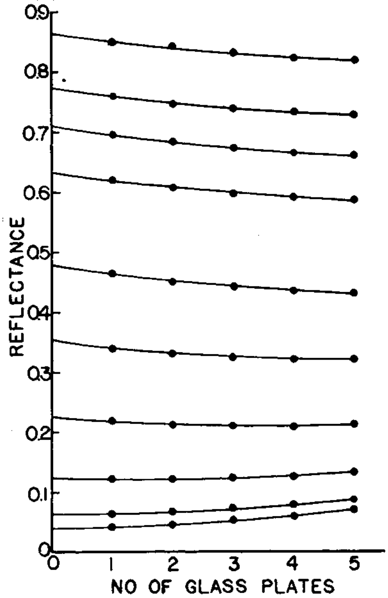

Fig. 4. Reflectance of a red sample plotted against the number of glass plates.

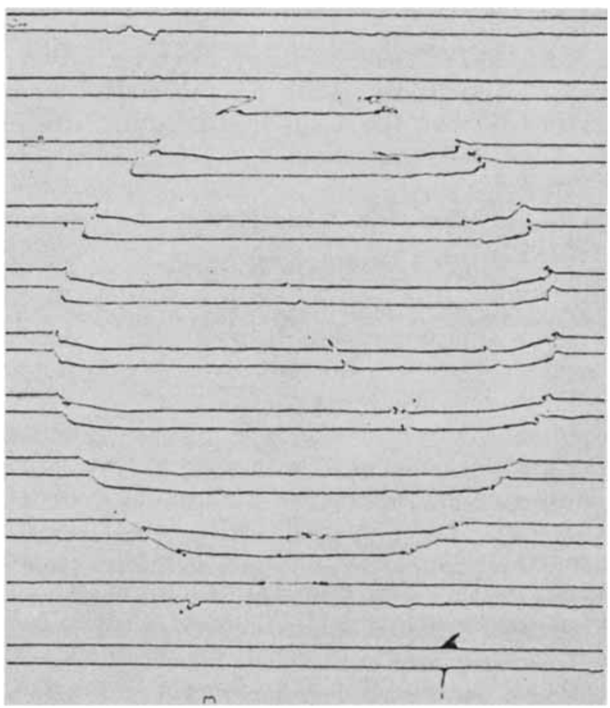

Fig. 5. First-order equidensities, produced from negative of a normal interference picture of a cross section.

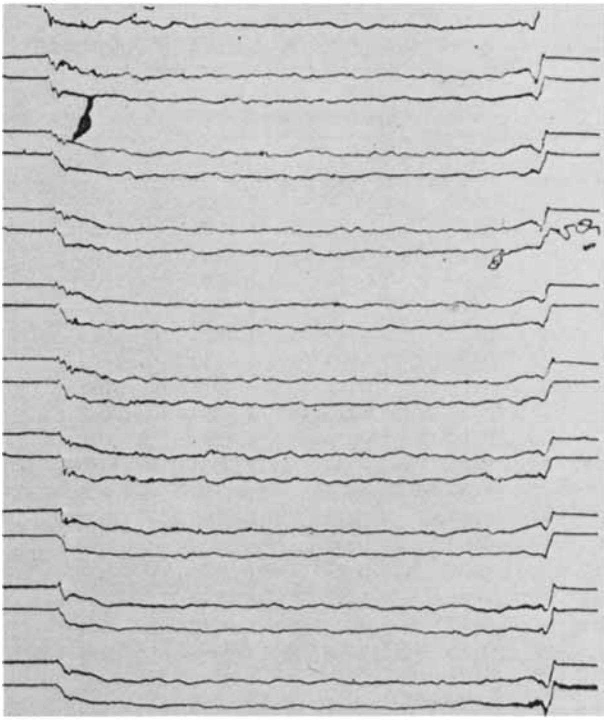

Fig. 6. First-order equidensity picture of a ringdyed sample, longitudinal section.

Effect of Dye Penetration on the Refractive Index of the Fiber

In the theoretical analysis, the refractive indices of the dyed and undyed portions of the filament were assumed to be the same. Otherwise, the light paths inside the ringdyed fiber would not be straight. Longitudinal and cross sections of 12 microns in thickness were cut from a red ringdyed sample on a sledge microtome with freezing attachment and mounted in an immersion oil for examination in a Leitz interference microscope. No effect of the dye on the refractive index was observed with monochromatic radiation at 436 nm. When radiation of 546 nm was used, the light path curved in the dyed portion (Figs. 5 and 6). A gradual change of refractive index with penetration will give the same effect. Significant light absorption occurs at 546 nm in the dye–fiber system with the red dye.

TREATMENT OF THE EXPERIMENTAL DATA

Some color was lost during the redistribution process. A correction was necessary in order to compare the reflectance of the redistributed sample to that of a ringdyed sample of the same dye content. The reflectances of the sample in which the dye was uniformly redistributed were measured at wavelengths from 380 to 700 nm in 10-nm increments (Table I) and converted to the corresponding CK values, as suggested by the relation obtained

TABLE I
Reflectance of a Fiber Bundle Dyed with C. I. Acid Red 1[a]

Wavelength, microns	Measured reflectance values			Corrected reflectance values	
	R_r	R_h	R_r/R_h	R_h	R_r/R_h
.45	.0665	.0603	1.1028	.041	1.6220
.46	.0593	.0540	1.0981	.039	1.5205
.47	.0545	.0483	1.1284	.038	1.4342
.48	.0500	.0463	1.0799	.038	1.3158
.49	.0478	.0440	1.0864	.038	1.2579
.50	.0465	.0420	1.1071	.038	1.2237
.51	.0450	.0405	1.1111	.038	1.1842
.52	.0443	.0395	1.1215	.0375	1.1813
.53	.0428	.0380	1.1263	.037	1.1568
.54	.0418	.0373	1.1206	.036	1.1611
.55	.0403	.0368	1.0951	.036	1.1194
.56	.0400	.0358	1.1173	.035	1.1429
.57	.0440	.0373	1.1796	.0355	1.2394
.58	.0605	.0495	1.2222	.046	1.3152
.59	.1003	.0838	1.1969	.077	1.3026
.60	.1615	.1448	1.1153	.135	1.1963
.61	.2385	.2220	1.0743	.211	1.1303
.62	.3110	.2995	1.0384	.294	1.0578
.63	.3723	.3615	1.0298	.364	1.0228
.64	.4178	.4093	1.0208	.412	1.0141
.65	.4593	.4490	1.0229	.445	1.0321
.66	.5028	.4885	1.0293	.488	1.0303

[a] Ring thickness in this case is 0.15 radii.

from the Allen and Goldfinger treatment. The *CK* values were multiplied by the reciprocal of the fraction of dye lost, giving new *CK* values which correspond to the values at no dye loss. These new *CK* values were converted back to reflectance values, which were assumed to be the reflectance values had no dye loss occurred. The ratio of the reflectance of the ring-dyed sample, R_r, to the corrected reflectance of the redistributed sample, R_h, was calculated at 10-nm intervals throughout the whole visible spectrum.

COMPARISON OF EXPERIMENT WITH THEORY

The ratio of the reflectance of the ringdyed sample to that of the uniformly dyed sample of equal dye concentration, R_r/R_h, is plotted against the reflectance of the uniformly dyed sample in Figures 7, 8, and 9. The values predicted by Allen and Goldfinger are shown in Figure 7. In order to make sure that the correction of the reflectance R_h for dye loss has not changed the general shape of the curve, similar plots were made using uncorrected values of R_h in Figures 8 and 9. The correction displaces the experimental points to higher value of R_r/R_h without changing the shapes of the curves. This shows that the agreement of the experimental results

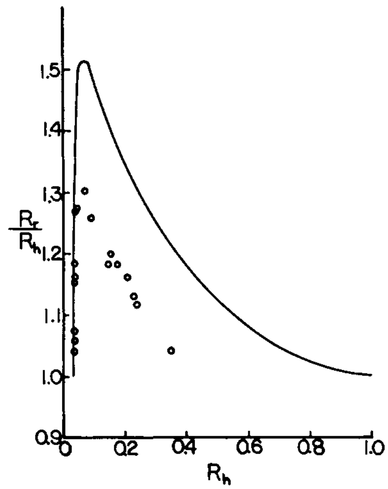

Fig. 7. Ratio R_r/R_h plotted against R_h for a red sample with ring thickness 0.1: (——) Allen and Goldfinger prediction (based on m, the refractive indices ratio, equal to 1.52); (O) experimental results.

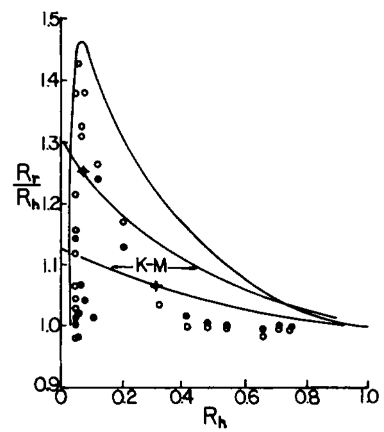

Fig. 8. Ratio R_r/R_h plotted against R_h for a red sample with ring thickness 0.125; (——) Allen and Goldfinger prediction; (K-M) Kubelka and Munk prediction made coincident with the points +; (●) experimental results using 0.95 as correction factor for the color loss; (O) experimental results corrected with different correction factors at corresponding wavelengths.

with the theoretical predictions is not an artifact arising from the correction processes.

According to the theoretical model of Allen and Goldfinger, a maximum value of R_r/R_h is to be expected at $R_h = 0.075$. Garrett and Peters' work[4] yields only three theoretical estimates of this ratio for a given ring thickness. Their predicted values are higher than those by Allen and Goldfinger and much higher than those observed. From the three predicted points, one cannot conclude whether or not there is a maximum value.

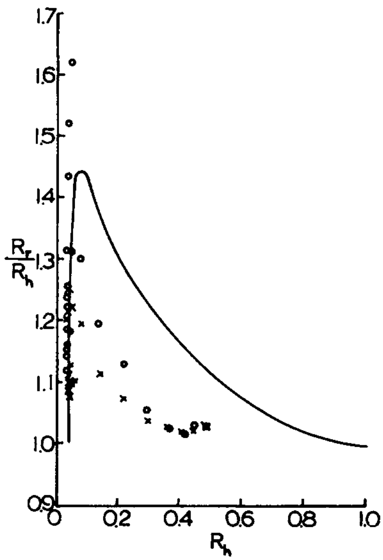

Fig. 9. Ratio R_r/R_h plotted against R_h for a red sample with ring thickness 0.15; (——) Allen and Goldfinger prediction; (×) experimental results without correction; (O) experimental results corrected for color loss at the corresponding wavelengths.

Two predictions based on the Kubelka and Munk treatment are shown in Figure 8. In the wavelength range in which no light is absorbed, there is no effect of the distribution of colorant. The ratio R_r/R_h is unity. If all the refracted light is absorbed, the reflectance is due only to the fiber surface. Assuming no change in the refractive index of the fiber, the ratio R_r/R_h must again be unity. At intermediate values of R_h, the ratio R_r/R_h could be greater or less than unity. Experiment shows the ratio R_r/R_h to be greater than unity and to be essentially as predicted by Allen and Goldfinger[2] and also by Garrett and Peters.[4]

The Kubelka and Munk treatment does not take into account the reflectance at the air–fiber interface. Therefore, at low reflectances, i.e., at high K/S values, one cannot expect valid predictions. However, the treatment also fails in the high reflectance range, in which the approach is supposed to be applicable.

The experimental curves had the general shapes predicted by Allen and Goldfinger,[2] but were located consistently at lower R_r/R_h values. This may be due to deviations between the experimental conditions and the assumptions of the theoretical model. Firstly, the model assumed parallel fibers separated from one another in such a way that the light reflected or refracted by a fiber should not be affected by its neighbors. In reality the fibers were closely packed. Secondly, the dye distribution across the fiber was different from the idealized one (Fig. 1). This diffuseness of the dye distribution should lead to smaller differences between the reflectances of ringdyed and uniformly dyed samples. Thirdly, the change of the refractive index of the dye–fiber system in the range of significant absorption was not considered.

It is believed that the primary purpose of this investigation, which was to provide an experimental test of the essential correctness of Allen and Goldfinger's theory of the color of scattering-absorbing substrates has been achieved and that at this stage of the study, mathematically difficult corrections of doubtful validity and importance are not justified.

CONCLUSIONS

For a given average dye concentration, the reflectance of a ringdyed fiber is higher than that of a uniformly dyed fiber. This can account for the increase in the depth of shade of an incompletely dyed substrate when it is subjected to treatment, such as heat setting or hot washing, which causes further dye penetration. By extending the Allen and Goldfinger treatment, this effect is predictable.

The experimental results support the essential correctness of the theoretical model. Although the predicted magnitudes of the effects are higher than those found experimentally, the location of the maximum effect is as predicted by the model.

Since this is a very sensitive test of a special case of the general theory, the evidence given here supports the validity of the general equations of the Allen and Goldfinger treatment.

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