

Steam and Heat Setting of Nylon 6 Fiber. II. Effects of Heat Setting of Nylon 6 Fiber on Dyeability and Fine Structure*

M. TSURUTA and A. KOSHIMO, *Research Institute, Nippon Rayon Company, Ltd., Uji City, Kyoto, Japan*

Synopsis

Drawn and undrawn nylon 6 fibers subjected to dry heat setting or steam setting were dyed with an acid dyestuff and a direct dyestuff. The dye uptake of these fibers was determined, and the rate of diffusion of a disperse dyestuff was evaluated by the method of Kramer. For the drawn nylon 6, the dye uptake and the diffusion coefficient are generally increased by the steam setting. This tendency increases with the temperature of the steam setting. However, dry heat setting up to about 160°C. gives the reverse tendency. In both types of setting treatments, the diffusion coefficient decreases with increasing tension of the sample during setting. For the undrawn nylon 6, the same effects of the heat setting are observed. Therefore the change of dyeability on steam setting is not attributable to a decrease in the orientation of crystallites but is caused by loosening of the molecular packing in the amorphous region as a result of inclusion of water. The change of dyeability resulting from dry heat setting, however, results from the increase in crystallinity and also closeness of packing in the amorphous regions.

1. INTRODUCTION

Few reports have appeared in which the relation between heat setting and dyeability of nylon 6 is investigated from the viewpoint of variation of fine structure. A. W. Eichells¹ reports that the uptake of acid dyestuff increases with setting temperature when nylon is subjected to dry heat setting at low temperatures for a short time. Yano² et al. report that at elevated temperatures the uptake of dyestuff increases owing to the decomposition of nylon. With high pressure steam setting above 100°C., nylon shows an increased affinity for acid, direct, and disperse dyestuff.³

In general, the dyeing properties involve the following three factors: the diffusion of the dye molecule in the fiber, the amount of dyestuff absorbed at saturation, and the difference in the standard chemical potentials of dyestuff in the dyebath and in the fiber, i.e., the affinity of dyestuff.

Investigation of dyeing properties is valuable as a means of estimating the internal structure of nylon 6 fiber, especially the state of the amorphous regions, since the dyestuff can penetrate only accessible parts of the amorphous region.

* This material appeared in part in *Kobunshi Kagaku*, **16**, 168 (1959).

In the present series of experiments, we investigated the relation between equilibrium uptake and the effect of molecular size of the dyestuff on the basis of the absorption curves for Azo Geranine 2G, an acid leveling dyestuff, and Sirius Supra Grey R, a direct dyestuff having larger molecular structure. Further, the diffusion coefficients of dyestuff were determined by Kramer's method.⁴ According to this method, the relation between the distance the dyestuff diffuses in nylon 6 gut and dyeing time is expressed by:

$$D = X^2/2t$$

where D is the apparent diffusion coefficient, X is the diffused distance of dyestuff, and t is the time. A plot of the diffused distance against square root of time gives a straight line through the origin.

2. EXPERIMENTAL

Measurement of Dye Absorption

Materials and Apparatus. As described in the first report,⁵ drawn nylon 6 fiber (100 den./24 filaments) and undrawn fiber were subjected to dry heat setting or steam setting and stored in a dry state.

As shown in Figure 1, dyeing was carried out in a three-necked flask fitted with a reflux condenser and a stirrer. The three-necked flask was

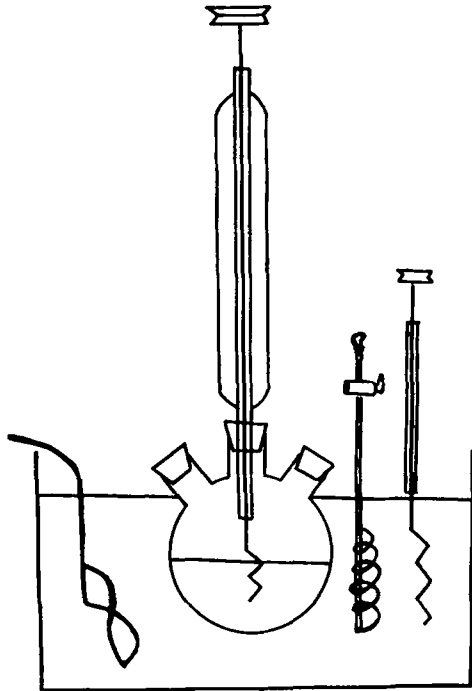


Fig. 1. Apparatus for measurement of absorption of dyestuff.

placed in a bath, which was maintained at 60°C. The nylon filament was cut into about 5 mm. pieces and put into the flask. The speed of rotation of the stirrer was 1000 rpm. Generally, errors in measurement of dye absorption were mainly attributed to differences in concentration of dye in the solution and on the surface of the fiber, as a result of insufficient agitation of the sample. This fact was already reported by Alexander et al.⁶ for dyeing of wool. A preliminary dyeing experiment on the rate of absorption of dyestuff on nylon with varying rates of stirring in the apparatus shown in Figure 1 confirmed that the effect of agitation on the rate of absorption of dyestuff to nylon was negligible at stirring speeds above 600 rpm. (Fig. 2).

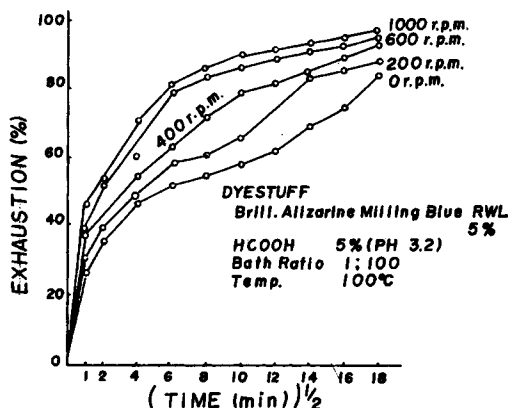


Fig. 2. Effect of stirring on exhaustion of dyestuff.

Dyeing. Azo Geranine 2G was used to investigate the equilibrium uptake of nylon. The method employed for purification was that of Wright⁷ and consisted in salting out with ammonium sulfate three times, recrystallizing from water to complete removal of SO_3^{-2} ion and then running the dye solution through a cation-exchange resin, Amberlite ER 120, to yield dye acids. After the solution of dye acids was concentrated at low temperature under reduced pressure, the crystal of dye separated was recrystallized from mixed solution of water, ethanol, and diethyl ether. With Sirius Supra Grey R, a commercial dye was used.

The dyeing conditions were as follows: the dyebath contained 500 mg. of dye/l.; the dyeing temperature was 60°C.; the liquor ratio was 100:1; the pH of the dyebath was 2.8 (in the case of Sirius Supra Grey R, pH was 7.0).

Estimation of Dye Uptake. After dyeing for a given time, the dye remaining in the dyebath was estimated colorimetrically with a photoelectric absorptiometer. Exhaustion of dye was plotted against the square root of the time.

Measurement of Diffusion Coefficient

Material and Apparatus. Undrawn nylon 6 gut of 10,000 den., which was the same as used in the first report⁵ for the measurement of bending modulus, was subjected to heat setting under the same conditions. Before dyeing, the sample was dried for several days.

The apparatus was the same as described above (Fig. 1). The samples were fixed on stainless wire and suspended in the liquid of the dyebath; this arrangement permitted the samples to be removed easily from the bath at a definite time.

Dyeing and Estimation of Diffusion Rate. The dyebath contained 2 g. of Dispersol Orange G/l.; dyeing was at 60°C.; the liquor ratio was 500:1 at the start of dyeing.

After dyeing for a given time, the samples were taken out, rinsed, dried, then cut into sections, and the depth of penetration of dye was measured by means of a micrometer. The diffusion rate was estimated by plotting the square root of the time against the depth of penetration.

3. RESULTS AND DISCUSSION

Absorption of Dyestuffs

Figure 3 shows that neither the rate of absorption nor the equilibrium exhaustion of Azo Geranine 2G in nylon 6 varies so greatly with conditions of heat setting as for Sirius Supra Grey R shown in Figure 4. This is attributed to the smaller size of Azo Geranine 2G molecule. With no heat setting, the absorption rates of the dyes in drawn fiber are lower than those in undrawn fiber since drawing, which is accompanied by a great increase in orientation, decreases the absorption rate of dyes beyond the inverse effect of increase of surface area with drawing. However, with steam setting, the absorption rate of the dye increases greatly with increasing setting temperature. With dry heat setting, the absorption rate of the dyes decreases with increasing setting temperature up to 160°C. and the influence is not so great as in the case of steam setting. These results are very interesting.

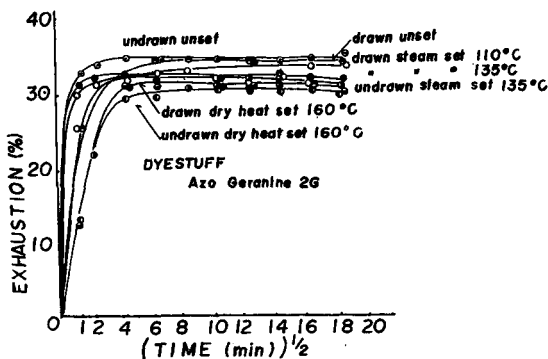


Fig. 3. Effect of heat setting of nylon 6 on rate of absorption of acid dyestuff.

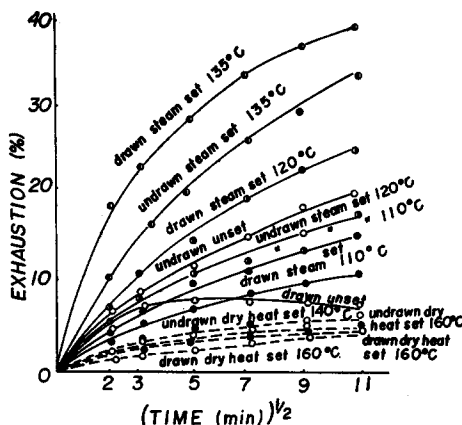


Fig. 4. Effect of heat setting of nylon 6 on rate of absorption of direct dyestuff.

In general, it is observed that heat setting causes increase in density and crystallinity and a decrease in the fraction of amorphous region where the dye is able to penetrate, so that absorption rate of dye is assumed to be smaller in heat-set fibers than in fibers receiving no heat treatment. In the present experiments, this effect of heat setting on absorption rate of dye was evidently observed in dry heat setting, whereas in steam setting the reverse effect was found, in spite of the greater increase in density compared to dry heat setting as reported in Part 1.⁵ The factors for this inconsistency are considered to be as follows: (1) the increase of absorption rate of dye owing to decrease of orientation beyond the inverse effect of the increase of crystallinity; (2) the increase in the number of amino endgroups owing to the hydrolysis of nylon molecules; (3) the increase of affinity of fiber for dyes; (4) the loose packing, i.e., the swelling of molecular aggregates in the amorphous regions owing to the presence of water molecule which prevents re-linking between nylon molecules after heat setting.

Considering factor (1), where energy in the form of heat is supplied, the thermal movement of the molecules is increased, and the disorientation of crystallite occurs. In fact, dry heat setting at above 190°C. decreases the orientation nearly to that of the undrawn state. This change in orientation affects the rate of absorption of dye favorably. However, this factor is considered not to be essential because of following results. Contrary to expectation, dry heat setting in this experiment decreases dye uptake. Also most important is the fact that the effect of dry heat setting on dye uptake of undrawn fiber is similar to that on drawn fibers, and further that the dye uptake of higher in drawn fiber subjected to steam setting at 120 and 135°C. is higher than that of undrawn unset fiber. The decrease of orientation with heat-setting was investigated by means of x-rays, and the results are reported elsewhere.⁸

If factor (2) is important the equilibrium exhaustion of Azo Geranine 2G shown in Figure 3 will be different in nylon fibers subjected to steam

setting at various temperatures. The higher the temperature at which steam setting is carried out, the higher the equilibrium exhaustion of dye should be, because Azo Geranine 2G binds with the amino endgroup of nylon stoichiometrically, as shown in the report of Peters.⁹ In this experiment, however, the equilibrium exhaustion of the dye decreased slightly with the increase of temperature of heat setting. This unexpected result is attributed to the decrease of available sites for dye owing to the occlusion of amino endgroups in crystals with the increase of crystallinity. The hydrolysis of nylon molecules must be investigated by means of measurement of viscosity in solution and determination of both amino and carboxyl groups. The result is also reported in another paper.¹⁰ However, it is presumed from this experiment that the factor (2) is not essential.

The change of affinity for dye anion in terms of factor (3) would be considered from the point of view of electromeric effects on amino endgroups which would be influenced by the change of crystallinity and of crystalline size, since a fiber molecule passes through several crystals. These electromeric effects on amino endgroups are thought not to affect so markedly the affinity for direct dyes as for acid dye, since the affinity for the former does not depend upon amino endgroup alone. Thus, the fact that absorption rates of direct dye in fibers subjected to steam setting under various temperatures are very different cannot be explained on the basis of factor (3).

Last of all, since the other three factors are not capable of explaining the data on absorption rate, the factor (4) is thought to be most essential, this is confirmed by the results shown in Figures 3 and 4. Namely, as the molecular length of Sirius Supra Grey R is about three times that of Azo Geranine 2G, diffusion of Sirius Supra Grey R takes place with much more difficulty than that of Azo Geranine 2G. In other words, the change of pore size in the amorphous region of the fiber subjected to heat setting is of such an order of magnitude as to affect the diffusion rate of dyes having different molecular size. In terms of the mechanism of steam setting, steam under pressure saturates the nylon fibers, i.e., water molecules having high energy penetrate between molecular chains and cause breakdown of intermolecular hydrogen bonds. When temperature is decreased under reduced pressure, formation of new hydrogen bonds among molecular chains is prevented by water molecule and the loose packing thus produced facilitates dye absorption.

Diffusion Rate of Dye

As shown above, the most remarkable effect of heat setting on dyeing properties is the change of rate of diffusion of dye. The diffusion coefficient of disperse dye having a small molecular weight was measured by use of Kramer's method. Assumptions (1)-(4) above, which predict a change of internal structure with heat setting, were confirmed on the basis of diffusion coefficient results.

In Figures 5 and 6 is shown the diffusion of dye into drawn or the undrawn samples subjected to dry heat setting or steam setting under relaxed

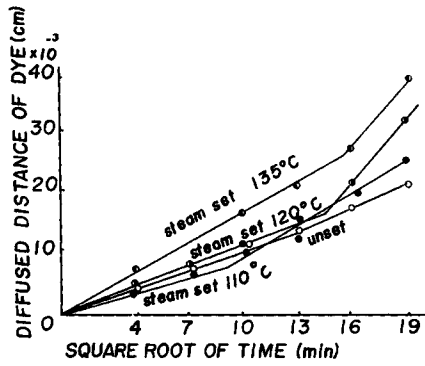


Fig. 5. Effect of dry heat setting and steam setting without tension on diffusion of Dispersol Orange G into undrawn fiber.

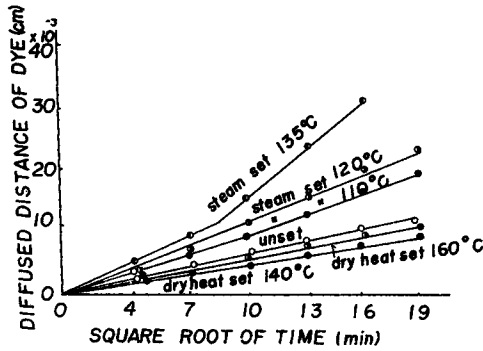


Fig. 6. Effect of dry heat setting and steam setting without tension on diffusion of Dispersol Orange G into drawn fiber.

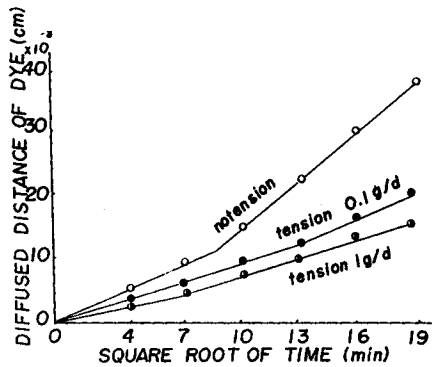


Fig. 7. Effect of tension on rate of diffusion of Dispersol Orange G into sample steam-set at 110°C.

conditions. Plots of the diffused distance against square root of the time show a straight line passing through the origin, so that the relation follows Kramer's equation. However, with steam setting, there is an inflection point. Up to this inflection point, differences in diffusion rates of the dyes

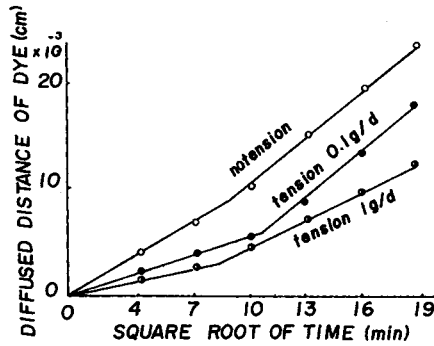


Fig. 8. Effect of tension on rate of diffusion of Dispersol Orange G into sample steam-set at 120°C.

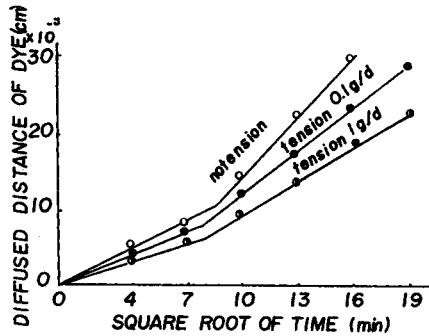


Fig. 9. Effect of tension on rate of diffusion of Dispersol Orange G into sample steam-set at 135°C.

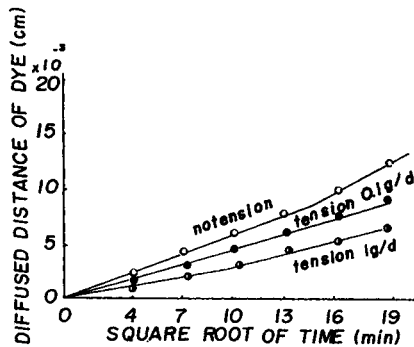


Fig. 10. Effect of tension on rate of diffusion of Dispersol Orange G into sample dry-heat-set sample at 160°C.

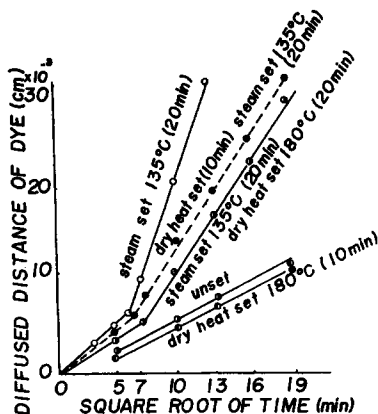


Fig. 11. Effect of alternating dry heat setting and steam setting on diffusion rate of Amacel Heliotrope I.

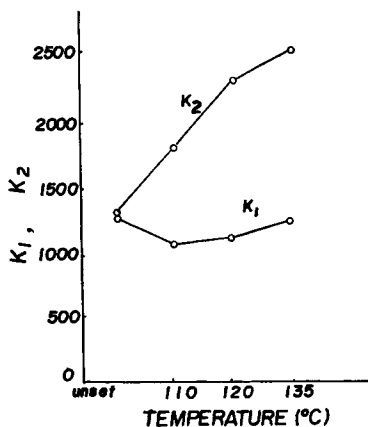


Fig. 12. Relation between temperature of steam setting and K_1, K_2 for drawn sample.

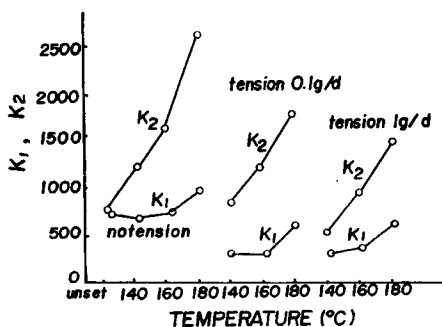


Fig. 13. Relation between temperature of dry heat setting and K_1, K_2 for drawn sample.

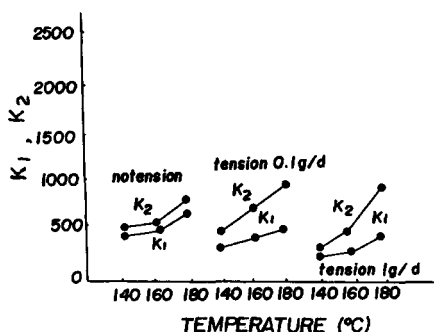


Fig. 14. Relation between temperature of dry heat setting and K_1 , K_2 for drawn sample.

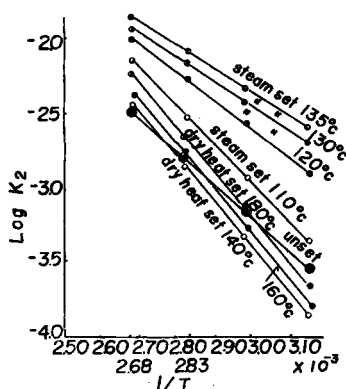


Fig. 15. Change of activation energy with conditions of heat setting.

in the samples subjected to various heat setting treatments are relatively small, while after this point the diffusion coefficient of the dyes increases markedly with setting temperature. Penetration of dye into undrawn sample takes place easily, so that the effect of heat setting on diffusion rate into undrawn fiber is not so great as in the case of the drawn fiber.

Figures 7–10 show the effect of tension during heat setting on diffusion rate of dye: the higher the tension, the slower the diffusion rate of dye. These differences in diffusion rate are readily explained by the looseness of packing predicted for the amorphous regions.

Figure 11 shows the diffusion of dye into the sample subjected to dry heat setting and then steam setting or vice versa. When the sample subjected to steam setting is reset with dry heat, the diffusion rate decreases, in agreement with the prediction of a second change in packing in amorphous region. It is concluded from the above that the increase of the diffusion rate with steam setting is not attributed to the decrease of orientation but the looseness of packing in amorphous regions. A sample first subjected to dry heat setting and subsequently to steam setting shows larger diffusion rate of dye than one subjected to dry heat setting only,

TABLE I
Activation Energies for Amacel Heliotrope I under Various
Conditions of Heat setting (Nylon 6, No Tension)

Heat setting		Temperature, °C.	Activation energy, kcal./mole
Type			
None			9.78
Steam setting		110	10.38
"	"	120	8.92
"	"	130	7.55
"	"	135	7.68
Dry heat setting		140	11.89
"	"	160	12.26
"	"	180	12.12

but the effect is not so great as that in steam setting only. It is shown from the above that the effect of dry heat setting cannot be reversed completely by subsequent steam setting. In order to make clear the effect of temperature and tension during heat setting on diffusion, we take constants K_1 and K_2 which are the slopes before and after the inflection point, respectively, in the curve of diffused distance of dye versus square root of the time. Both K_1 and K_2 are thought to be proportional to the diffusion rate of dye which was obtained by means of Kramer's method. The relations between these values and conditions of heat setting are shown in Figures 12-14. Figure 15 shows the plot of the logarithm of K_2 for the sample subjected to various conditions of heat setting against reciprocal of the absolute temperature of dyeing. Amacel Heliotrope I was used in order to give distinctive front of dye diffused. The apparent activation energy for diffusion of dye was calculated from the value of this slope based on the Arrhenius equation. As shown in Table I, the activation energy for diffusion decreases with increasing temperature in steam setting. It is seen from this result that steam setting facilitates the diffusion of dye. On the

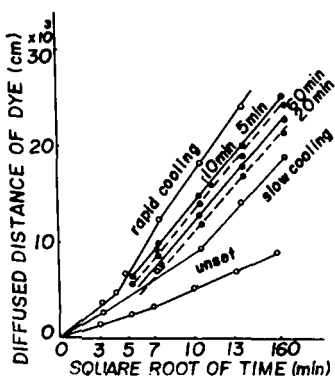


Fig. 16. Effect of cooling rate after steam setting on diffusion rate of Amacel Heliotrope I.

other hand, a larger activation energy for the diffusion of dye into the sample subjected to dry heat setting is observed, and this corresponds to a decrease in rate of dyeing with dry heat setting.

The inflection point in plots of the diffused distance of dye against the square root of time appears at 15×10^{-3} cm. and $5-10 \times 10^{-3}$ cm. for the undrawn and the drawn samples, respectively, except in the case of dry heat setting. The positions of these inflection points in the samples subjected to steam setting indicate that water penetrating into the sample under high temperature and pressure would be enclosed in the fiber as a result of shrinking of the fiber under a sudden drop in pressure, thus causing loose packing in the fiber. Figure 16 shows the effect of the rate of cooling of the sample subjected to steam setting on the inflection point: the slower the cooling rate, the larger the diffused distance of dye at inflection point. This observation supports the above assumption.

4. CONCLUSION

The increased dyeability of nylon 6 fiber owing to steam setting is not attributed to disorientation of crystallite, but to loose packing of nylon molecules in the amorphous region. The decreased dyeability resulting from dry heat setting is attributed to a decrease in extent of the amorphous regions accompanied by an increase of crystallinity and also close packing, i.e., bonding of nylon molecules after dry heat setting is facilitated by the absence of water molecules.

Further, heat setting under tension prevents the disorientation of crystallites and restricts free movement of nylon molecules in amorphous regions to reduce pore size, especially in dry heat setting, so that the diffusion of dye may be decreased.

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Résumé

Les fibres de nylon 6 étirées et non étirées soumises à la prise par la chaleur sèche ou par la vapeur, sont colorées par un colorant acide et par une matière colorante directe. La teneur en colorant de ces fibres fut déterminée et la vitesse de diffusion d'une matière colorante dispersée fut évaluée par la même méthode que celle employée par Kramer.

Sur le nylon 6 étiré, le teneur en colorant et le coefficient de diffusion augmentent généralement par la prise au moyen de la vapeur. Cette tendance devient remarquable avec la température de la prise à la vapeur. Dans ce cas, l'augmentation de la tension employée dans le traitement réduit le coefficient de diffusion. Cependant la fixation par la chaleur sèche à environ 160°C, donne la tendance inverse excepté pour l'effet de la tension. Sur le nylon 6 non étiré, les mêmes effets de la fixation par la chaleur sont observés.

C'est pourquoi, le changement des propriétés colorantes par la prise à la vapeur est causé non par la décroissance de l'orientation des cristallites mais par l'entassement moindre de la structure intermoléculaire dans la région amorphe débarrassée d'eau. Tandis que le changement des propriétés colorantes par la prise au moyen de la chaleur sèche est causée par l'augmentation de la cristallinité et aussi par l'entassement étroit dans la région amorphe.

Zusammenfassung

Trockenhitze- oder dampfbehandelte, gereckte und ungereckte Nylon-6-Fasern wurden mit einem sauren und einem direkten Farbstoff gefärbt. Die Farbstoffaufnahme dieser Fasern wurde bestimmt und die Diffusionsgeschwindigkeit eines Dispersionsfarbstoffes durch die Kramer'sche Methode ermittelt. Beim gereckten Nylon-6 nahm die Farbstoffaufnahme und der Diffusionskoeffizient im allgemeinen bei Dampfbehandlung zu. Diese Tendenz wurde mit zunehmender Temperatur der Dampfbehandlung augenfällig. In diesem Falle verringert die Zunahme der bei der Behandlung verwendeten Spannung den Diffusionskoeffizienten. Dagegen besteht bei Trockenhitzebehandlung bis zu etwa 160°C, mit Ausnahme des Spannungseinflusses, die umgekehrte Tendenz. Bei ungerecktem Nylon-6 beobachtet man den gleichen Einfluss der Hitzebehandlung. Deshalb ist der Grund für die Änderung der Färbereigenschaften bei Dampfbehandlung nicht eine Abnahme der Kristallitorientierung, sondern die Lockerung der Packung der intermolekularen Struktur in den amorphen Bereich durch Wasser. Die Änderung der Färbereigenschaften bei Trockenhitzebehandlung wird durch Zunahme der Kristallinität und auch durch die dichtere Packung im amorphen Bereich verursacht.

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