*Structural Heterogeneity in Viscose Fibers**

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Though various theories as to the cause and nature of the skin-core effect in viscose fibers have been advanced, none seems to be entirely satisfactory to accout for all the facts so far observed. On the other hand, some observations have been presented which show that the actual structures are far more complicated than the skin-and-core model[1~5], but the results obtained are not yet conclusive.

Dyeing properties of the fiber sections have been studied by various workers, who have dealt almost exclusively with the differential staining of the skin and core. This phenomenon is, as Hermans[6] pointed out, due to a more rapid diffusion of the dye into the core than into the skin.

Generally, dyeing property has two major factors. These are dye diffusion velocity and dye equilibrium absorption. If the picture is oversimplified it would seem that the dye equilibrium absorption is connected with the total spatial per cent of amorphous areas but the dye diffusion velocity is connected with the size and distribution of amorphous areas or the average orientation of the chains in these areas. Then the structural factor which causes the differences in velocity of dye diffusion should not always be identified with that which causes the differences in equilibrium absorption of dye. This suggestion is proved in various experiments.

In addition to the dyeing property of fiber section based on diffusion velocity, therefore, the situation at sorption equilibrium should also be studied. As for this subject, an interesting contribution has been published by Hermans[6], but it seems that there is possibility of further study.

The present investigation is concerned with (1) the observation on the dyeing property of fiber sections and (2) a study of the radial structural gradient by a peeling-off method.

Dyeing Experiment of Fiber Sections

As is well known in ordinary dyeing, the amount of dye absorbed is not sensitively reflected to the depth of color shade beyond the range of fairly low degrees of absorption. In order to distinguish clearly a difference in depth of stained shade on the cross sections prolonged-dyed, dyeing should then be carried out with a diluted dye solution.

Cross sections mounted in the usual way on slides, were dyed for long periods at room temperature with Oxamine Blue 4R which was purified by chromatographing on silica gel.

* Presented before the Meeting of the Fiber Society of Japan, held at Osaka, May 16, 1957.

1) M. Horio et al., *Textile. Research J.*, **17**, 264 (1947).
2) R. L. Royer and C. Maresh, ibid., **17**, 477 (1947).
3) G. G. Taylor and J. C. Brown, *J. Soc. Dyers & Col.*, **69**, 396 (1953).
4) G. D. Joshi and J. M. Preston, *Textile Research J.*, **24**, 971 (1954).
5) K. Kato, *Science [Japan] (Kagaku)*, **25**, 41 (1955).
6) P. H. Hermans, *Textile Research J.*, **18**, 9 (1948).

Müller-bath-type Fiber.—The fiber used here was an ordinary rayon (No. 1) spun in a bath containing sulfuric acid 110 g./l., sodium sulfate 350 g./l., and zinc sulfate 15 g./l.

After half an hour of dyeing in a solution of 0.3% Oxamine Blue 4R to which 1% of sodium sulfate had been added, the cross section exhibited the differential staining of skin-and-core with a selectively stained core, as is well known already. This is shown in Fig. 1.

As the dyeing time increased, the intensity of the color increased over all the parts, especially at both the outer circumference of the skin and the boundary between skin and core. After prolonged dyeing—for example, after dyeing for 6 hr. the section showed a finer staining differentiation than the skin-and-core, as shown in Fig. 2. In the section, a narrow zone of the core next to the skin exhibited a darker shade than the central part and was separated from the latter by a rather sharp boundary, and then showed up as a dark band. Moreover, the outer circumference of the skin was seen to stain deeply, but this zone was so thin that it was difficult to distinguish its existence.

Even after further dyeing the above fine differentiation remained, although it was very difficult to distinguish the differences in depth of color shade because of the intensive staining over the whole section.

When such intensively dyed sections were washed with water, the stain was seen to bleed easily off the outermost thin zone and the core but to remain in the main part of the skin. After short washing, the clearness of the boundaries among the various zones became pronounced and the multilayer-like differential staining came again into view. Fig. 3 is a micrograph of such partially washed-out sections mounted in water. As to the phenomenon that by short washing a narrow zone of the core next to the skin became pronounced, drawing a dividing line from the central part, a similar fact was observed already by Hermans, who did not interpret this narrow zone as the differentiated layer different from the central part, but then explained that during washing the former discolored much later than the latter. On the basis of the above observations on both dyeing and washing, however, it seems rather reasonable to assume that the narrow zone has a much greater dye equilibrium absorption than the central part and that there is, moreover, no remarkable difference in velocity of dye diffusion between the two. In the swollen sections in Fig. 3, a very thin deeply-stained outermost zone seems to be seen, but not yet clearly.

When washing had been carried further, the dye disappeared completely from both the outermost thin zone and the core, and remained only in the main part of the skin. Fig. 4 is a micrograph of such a washed-out section after immersion in water, photographed with a contrasting light filter. There is no doubt that a very thin outermost layer exists actually at the outside of the skin, free from the refraction and diffraction effects associated with the cellulose/water interface, as shown previously by Preston and Joshi[7]. This thin outermost layer has a high velocity of dye diffusion and a great dye equilibrium absorption (proved in the next section) and then exhibits a similar property towards dyes as a narrow zone of the core next to the skin.

The above-mentioned phenomena were also observed in other Müller-bath-type fibers (see Fig. 5) and with other dyestuffs such as Sky Blue FF.

In Müller-bath-type fibers there are apparently four distinct layers which differ in dyeing property. The skin itself is composed of two layers which differ in dye equilibrium absorption, and so does the core. These are summarized in Table I.

TABLE I. DYEING PROPERTIES OF FOUR LAYERS IN MÜLLER-BATH-TYPE FIBER
(in cross section)

Layer		Velocity of dye diffusion	Equilibrium dye absorption
Skin	1st layer	rapid	high
	2nd layer*	slow	low
Core	3rd layer	rapid	high
	4th layer	rapid	low

* The main part of the skin.

Skinless-type Fiber.—For a sample "Shintoramomen" (No. H-T) was used, which was a high tenacity rayon staple spun from low-alkali viscose in zinc-free and low-acid bath. Fiber of this type is marked by an all-skin structure, as shown in Fig. 6.

Fig. 7 shows a similar section washed-out after prolonged dyeing. In the section, the stain is seen to bleed completely off the outermost thin layer but to remain

7) J. M. Preston and G. D. Joshi, *Kolloid-Z.*, **122**, 6 (1951).

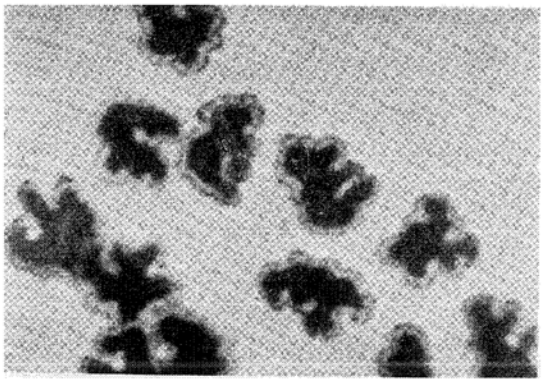

Fig. 1. Cross sections of an ordinary rayon (No. 1), dyed for 30 min. with Oxamine Blue 4R, mounted in canada balsam (×720).

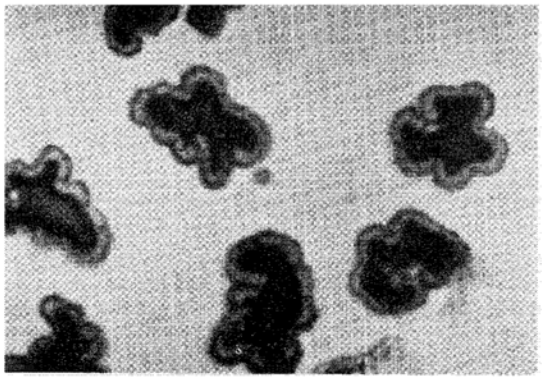

Fig. 2. Same as Fig. 1, except that the dyeing time was prolonged to 6 hr. (×900).

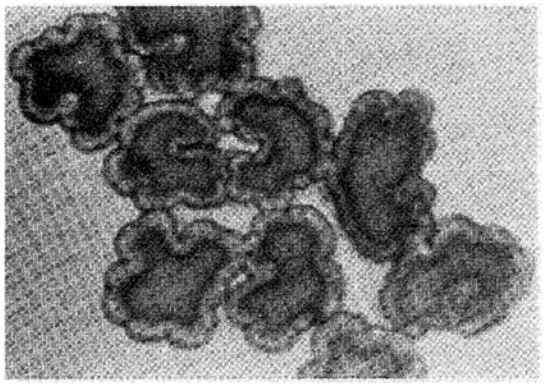

Fig. 3. Partially washed-out sections of an ordinary rayon (No. 1) pre-dyed intensively, mounted in water (×900).

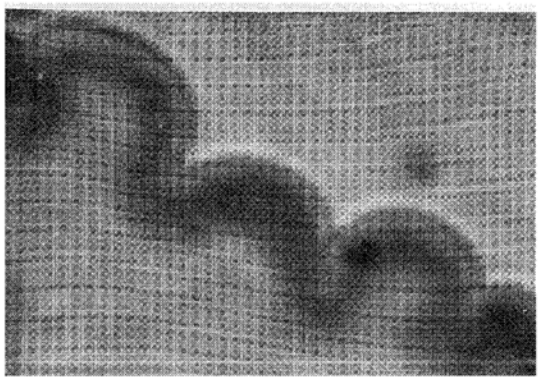

Fig. 4. Same as Fig. 3, except that washing was carried out further, whereas the dye was fixed only in the main part of the skin; mounted in water and examined by a oil-immersion objective (×2000).

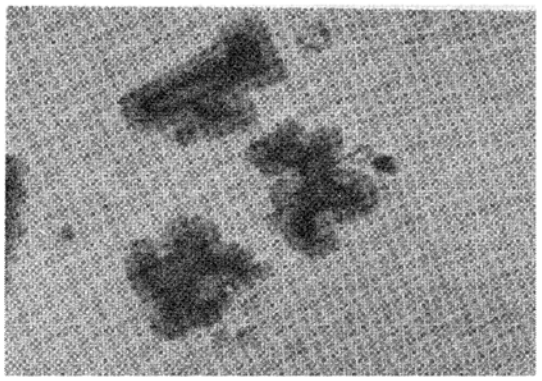

Fig. 5. Cross sections, of a tire-cord yarn, prepared as in Fig. 3 (×900).

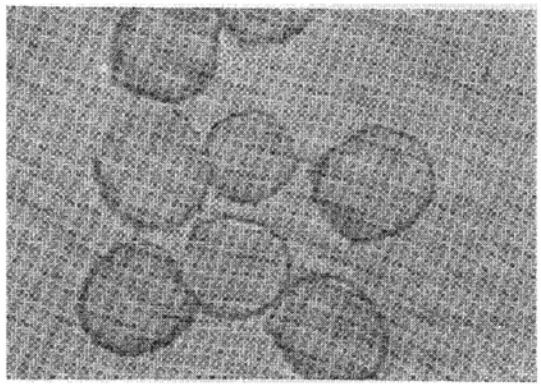

Fig 6. Cross sections of "Shintoramomen" (No. H-T), prepared as in Fig. 1 and mounted in canada balsam (×900).

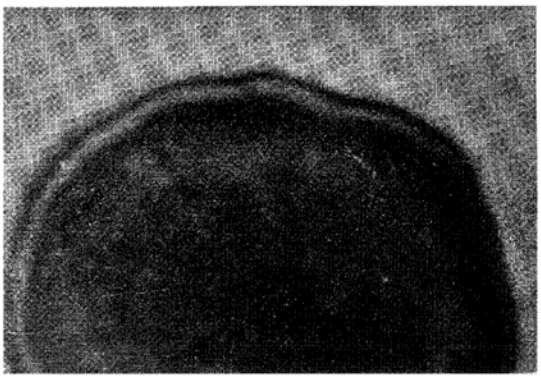

Fig. 7. Same fibre as in Fig. 6; section prepared as in Fig. 4 and mounted in water (×2000).

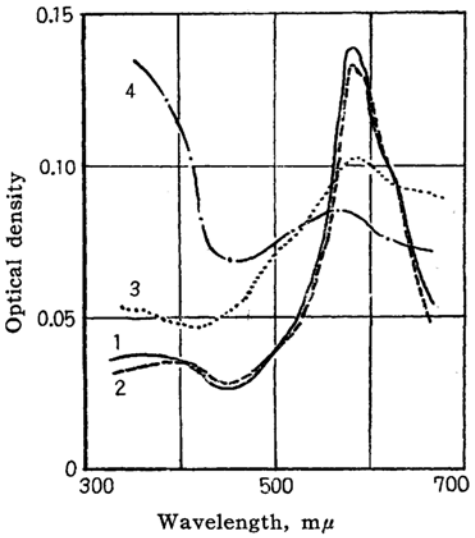

Fig. 8. Spectral sorption curves of dye solutions extracted from (1) the original fiber dyed with Japanol Brilliant Blue 6BKK, (2) the pre-dyed fiber peeled-off to *Pr* 0.23 (before nitration the pre-dyed fiber was vacuum-dried), (3) the pre-dyed fiber peeled-off to *Pr* 0.20 (before nitration the pre-dyed fiber was not vacuum-dried), and (4) the dyestuff decomposed by nitric acid.

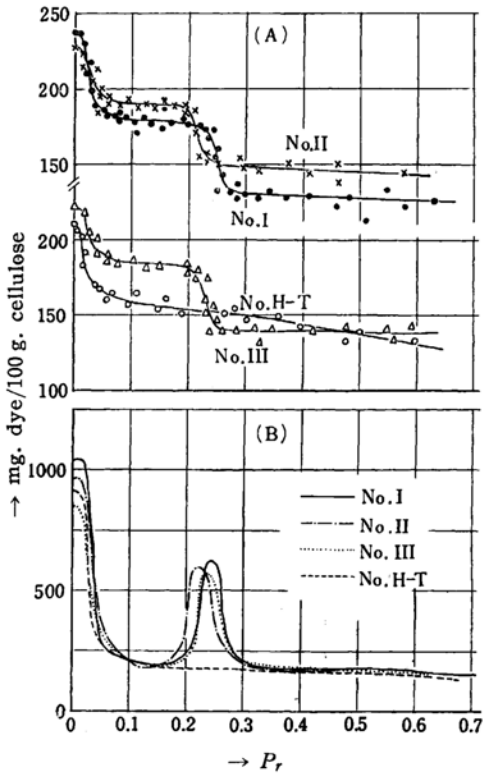

Fig. 9. (A) Amount of dye absorbed as a function of *Pr*. (B) Radial distribution curves in dye equilibrium absorption.

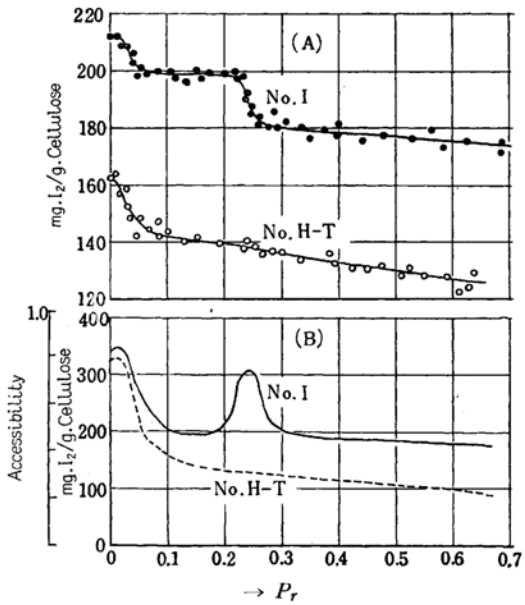

Fig. 10. (A) Amount of iodine absorbed as a function of P_r. (B) Radial distribution curves in iodine absorption and accessibility.

in the inner part, and then two distinct layers are clearly distinguishable. These two layers seem to correspond to the outermost and the second layer in the Müller-bath-type fiber, respectively.

Experiment with Peeling-Off Method

In view of the preceding observations it would seem that the actual structural heterogeneity is far more complicated than that assumed on the basis of the old skin-and-core model. In an investigation with peeling-off technique, therefore, it is necessary to peel the successive layers off as close as possible from the fiber surface toward the center and then to seek the nature of the radial structural gradient existing in fiber to the minutest details.

As a peeling-off technique the heterogeneous nitration presented by Okajima et al.[8] was applied. In a study of this kind, the point is in whether peeling-off is carried on successfully or not. Thereupon, numerous control experiments were carried out carefully.

Experimental Procedure.—A sample of fibers was thoroughly unraveled and vacuum-dried just before use (weight is W). Heterogeneous nitration was carried out at 18°C, and moisture was prevented from entering the reaction vessel. The nitration mixture was made from dry reagents and its composition was as follows:

Nitric acid (1.53) 3 g.
Acetic anhydride 3 g.
Carbon tetrachloride 90 g.
} per 0.5 g. sample.

After nitrating the samples to the desired degree, they were washed enough with dry carbon tetrachloride, vacuum-dried and then treated with acetone for removing the nitrate layer.

After applying fresh acetone, they were washed with NH_4SH alcoholic solution recommended by Okajima for the removal of the residual nitrate groups from the fiber surface. Finally they were washed with water, vacuum-dried and weighed (W').

The degree of peeling-off (Pr) was given on the base of the original radius of the filament and obtained by $Pr=1-(W'/W)^{1/2}$.

In order to direct operations properly, microscopical examination of cross sections of the nitrated fibers was carried out using the staining technique. When nitration was carried on much longer, it was seen that the nitrated layer began to show more and more radial flaws, and that nitration proceeded in an irregular fashion. In order to avoid a drawback of this kind, the reaction time was limited to half an hour. If a greater degree of peeling-off was desired, the sample was peeled-off with acetone and then exposed a second time to the nitrating mixture.

Because of the necessity of studying a radial distribution of dye in the dyed fiber—this is the main object in the present investigation — the application of the above peeling-off method to the dyed sample was examined. Fig. 8 shows spectral sorption curves of the dye solutions extracted from the original and peeled-off predyed samples. This figure indicates that, if nitration proceeds under absolutely dry conditions, the dye which remains in the unreacted part has not been decomposed and the acid has not diffused into the inner part beyond the nitrated layer. It was found eventually that the dyed sample was peeled-off satisfactorily as well as the undyed sample. In this case, however, water should not be used for washing, because the dye absorbed in the unreacted part was dissolved away with water.

Samples.—The fibers selected for investigation were "Shintoramomen" (No. H-T) and three ordinary rayons (No. I—III). No. I—III were all spun in the same Müller bath; 1.5, 3.0 and 7.0, deniers, respectively.

Radial Distribution in Dye Equilibrium Absorption.—A sample was dyed to equilibrium at 25°C in a solution of 0.001% Japanol Brilliant Blue 6BKX to which 0.2% of sodium sulfate had been added, and washed briefly with water to remove the mechanically absorbed dye from the fiber surface, vacuum-dried and then peeled-off. In Fig. 9-A is given the amount of dye absorbed as a function of the degree of peeling-off. The radial distribution curves derived therefrom are shown in Fig. 9-B. These are in good agreement with the differential staining based on the differences in equilibrium absorption, irrespective of the differences in dyestuff and even in procedure of dyeing (Ref. Figs. 2, 3 and 7). The fact that a very thin outermost layer has a greater dye equilibrium absorption is experimentally proved here.

Radial Distribution in Crystallinity.—Using the Hessler and Power's method[9], the radial distribution in accessibility was first studied. In Fig. 10-A are given the amount of iodine absorbed on the fibers peeled-off to various degrees. The radial distribution curves derived therefrom are shown in Fig. 10-B, in which a ratio of the absorption value to 412** gives a value for the accessible fraction. Four layers in Müller-bath-type fiber and two in Shintoramomen are clearly distinguished also here.

The accessibility thus obtained is, however, due to the inner surface areas for absorption and seems to be an unsatisfactory measure for crystallinity. In order to seek conclusive evidence on the nature of the fine structure in each layer, the lateral-order (L.O.) distribution of each separated layer was further determined according to the hydrocellulose solubility method presented by Maeda[10]. For example, the L.O. of the outermost layer of No. 1 (P_r: 0∼about 0.05) was determined by calculation from the L.O. of the original fiber and the observed L.O. of the fiber peeled-off to 0.05 (the outermost layer just about

8) S. Okajima et al., This Bulletin, **26**, 322 (1953).

9) V. J. Hessler and R. E. Power, *Textile Research J.*, **24**, 822 (1954).

** The milligram of iodine absorbed per gram of methocel, as the sample of the completely amorphous cellulose.

10) K. Maeda, *J. Soc. Text. Cellulose Ind. Japan* (*Sen'i-Gakukai-shi*), **12**, 10 (1956).

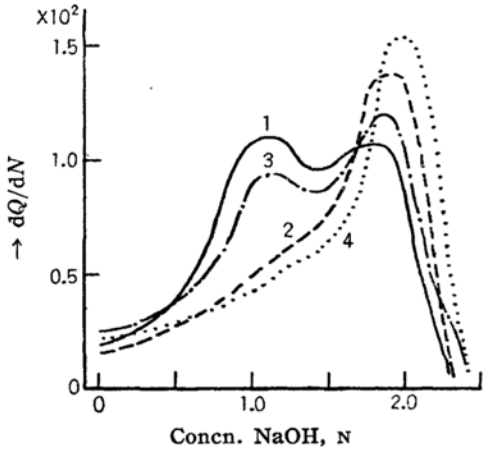

Fig. 11. L.O. distribution curves of each layers in No. No. 1.
(1) The outermost layer (P_r: 0～ca. 0.05). (2) The second layer (P_r: ca. 0.05～ca. 0.20). (3) The third layer (P_r: ca. 0.20～ca. 0.28). (4) The fourth layer (P_r: ca. 0.28～).

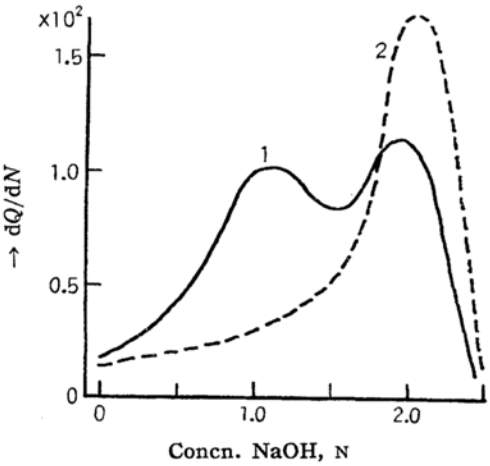

Fig. 12. L.O. distribution curves of each layers in No. H-T.
(1) The outermost layer (P_r: 0～ca. 0.05). (2) The second layer (P_r: ca. 0.05～).

removed). The results are shown in Figs. 11 and 12.

As is seen in the figures, there is an intrinsic difference in L.O. distribution between a layer with greater dye equilibrium absorption and that with less dye equilibrium absorption. The former has two peaks in its distribution curve and, consequently, lower crystallinity. The latter, on the other hand, gives only one peak in the region of considerably high order and, consequently, higher crystallinity. These are in agreement with the information obtained from the radial distribution in iodine absorption described before.

Discussion

As is seen from the above observations, there are two types of differentiated layers.

One is a layer rich in disordered material which shows a lower crystallinity and a greater dye equilibrium absorption. Cellulose gel of this type, which will be termed here "α-type", is formed by a momentary gelatinizing action, such as that of zinc ions[11].

The other is a highly crystallized layer with relatively limited amorphous regions and shows less dye equilibrium absorption. Cellulose gel of this type, which will be termed "β-type", is formed by a relatively slow gelatinizing action, such as those of sodium or hydrogen ions[11].

Consequently, it seems reasonable to assume that viscose fibers consist of the alternative succession of the α-type and β-type layers. In the Müller-bath-type fiber there are four successive layers, i.e., the α_1-, β_1-, α_2- and β_2-layer; the α_1- and β_1-layer altogether correspond to the skin, and the α_2- and β_2-layer to the core. This seems to be in agreement with the result of Joshi and Preston[4], who observed four zones which differ in transverse orientation.

As to the layer succession, there are some interesting facts as follows: (1) Fiber spun in a zinc-free bath has only one combination of the α-type and β-type layer, but fiber spun in a zinc-containing bath has double combinations. (2) The periods of the layer succession are identical in all fibers spun in the same composition of bath, irrespective of the differences of their deniers. These facts seem to lead to the suggestion that the bath composition is of essential importance for the occurrence of the Liesegang-like periodic coagulation which influences the rate of primary gelatination and, consequently, the degree of crystallization.

Moreover, all types of fiber have the outermost thin α-type layer, which will be designated "the cuticle layer"***, irrespective of the existence of zinc salt in their spinning bath. The formation of this layer seems to connect with some inevitable effect occurring when viscose contacts with bath liquid, — maybe, a momentary dehydration carried out in the

11) A. Nakai, ibid., **14**, 905 (1958); **15**, 9, 90, 166, 170 (1959).
*** The cuticle layer was shown also by Heyn, *Textile Research J.*, **27**. 449 (1957). Heyn's paper had not been published when the present investigation was presented at Spring Meeting of the Fiber Society of Japan, held on May 16, 1957.

order of the relaxation time of the macromolecules in viscose, on the surface of the extruded viscose[11].

The most noticeable conclusion to be drawn from the present study is that the main part of the skin has a good crystallinity as well as the central part. This is opposed to the opinions given in the majority of previous works, which maintain that the degree of crystallinity is less in the skin than in the core[12-14]. On the other hand, a few contributions have been reported which show that there is no remarkable difference in crystallinity between the two[15,16]. Since the actual differentiations are far more complicated as proved here, it is doubtful whether the actual nature of the structural heterogeneity can be sought by the methods used in previous works, for example, by a comparative study of the crystallinity of thick- and thin-skin fibers, or by that of the physical properties of fibers peeled-off to various degrees which kept a relatively long interval between the various ones.

The structural difference based on crystallinity is the major factor which causes the differences in dye equilibrium absorption, but not the major factor which causes the differences in velocity of dye diffusion. This is demonstrated by the following facts: (1) There is a remarkable difference in velocity of dye diffusion between the β_1- and β_2-layer, irrespective of the small difference in their crystallinities. (2) There is no difference in velocity of dye diffusion between the α_2- and β_2-layer, irrespective of the great difference in their crystallinities. Consequently, the skin-core effect is not, as Morehead and others believed, due to the differences in degree of crystallinity between the two.

As already shown by various works, the skin part has a higher degree of axial orientation than the core. Accordingly, the main part of the skin (the author's β_1-layer) seems to have a denser structure with good orientation and good crystallinity. The difficulty of the dye permeating into the main part of the skin, and, more generally, the skin effect seems probably to be due to the interdependence of its higher orientation and higher crystallinity.

The course of fiber formation from viscose seems not to be so simple as to be suggested by previous theories. The present investigation seems to demonstrate that some as yet unknown peculiarity in the process of diffusion of the bath components into the viscose is mainly responsible for skin formation.

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12) F. F. Morehead and W. A. Sisson, *Textile Research J.*, **15**, 443 (1945).
13) N. H. Chamberlain and M. P. Khera, *J. Textile Inst.*, **43**, T123 (1952).
14) T. Yurugi, *J. Chem. Soc. Japan, Ind. Chem. Sec. (Kogyo Kagaku Zasshi)*, **58**, 27 (1955).
15) P. H. Hermans, *Textile Research J.*, **20**, 553 (1950).
16) I. Sakurada and Y. Nukushina, Meeting of the Research Institute of Artificial Fibers, Japan (Oct. 1956).