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# Stabilization of Viscose Rayon by Heat Treatment by Means of Ammoniacal Preswelling Bath

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## INTRODUCTION

In the two previous papers of this series,[1,2] it was shown experimentally that viscose rayon shows most markedly the effects of stabilizing heat treatment, as exhibited by various physical and mechanical properties after being preswollen in sulfuric acid or acetic acid baths at the pH optimal for maximal hydration and heat-treated at a temperature near or just above the glass transition temperature of regenerated cellulose, i.e., around 70°C.

The present paper is concerned with the results of an experimental study in which ammonium hydroxide was used as the swelling agent. The $NH_4OH$ was chosen because, being volatile, it remains less in the fibrous structure during the heat treatment; and also, because, at the pH range optimal for hydration of cellulose, cellulose is expected to swell more in aqueous ammonium hydroxide.[7]

Also, attention has been given to the effect of desiccation of the preswollen samples, since the swelling of a sample, as noted in the previous paper, may be decreased depending on the degree of desiccation prior to heat treatment.

## EXPERIMENTAL

### 1. Original Sample of Viscose Rayon

The original sample of viscose rayon used and the method of purification were the same as described in the previous papers.[1,2] It was stored in a desiccator over $CaCl_2$ for about one week prior to treatment.

### 2. Pretreatment of Fibers

*a. Pretreatment in Ammonium Hydroxide Solutions*

A series of aqueous ammonium hydroxide solutions was so prepared that the pH of the solutions after the swelling equilibrium was attained was 7.0, 8.0, 9.0, 10.0, and 11.0, respectively. In each case a 3-g. sample reeled loosely on a glass frame was soaked in solution (1500 cc.) for 24 hr. at 25°C., after which the pH was determined. For comparison, a sample preswollen in an acetic acid bath (pH = 3.0) was also prepared as described in the previous paper.[2]

*b. Desiccation of Sample Prior to Heat Treatment*

Each of the preswollen fiber samples was then squeezed and vacuum- or air-dried at room temperature for various periods so that a series of samples of various degrees of desiccation was obtained.

*c. Heat Treatment*

Temperatures of 70–160°C. were used for the heat treatments, and a paraffin bath was used as an inert heating medium, as described in the previous papers.[1,2] The procedure of the heat treatment and of handling the heat-treated fibers was nearly the same as in the experiment given in the previous papers; after being removed from the paraffin bath, each of samples was extracted successively with petroleum ether (36 hr.) and a benzene–alcohol (1:1) mixture (36 hr.), this being followed by air drying at 25°C. for 2–3 hr. and storing in a desiccator over $CaCl_2$ for one week prior to the following tests.

### 3. Examination of the Effects of Stabilizing Treatments

*a. Breaking Properties*

Bundles containing 60 filaments were stored in a desiccator over a sulfuric acid solution of 55% R.H. for five days before being subjected to stress-strain measurements. Measurements were made at 25°C. at 60% R.H.; the specimen length was 20 mm. and the rate of elongation 1 mm./23 sec.

A constant-speed fiber tester designed in our laboratory[3] was used for stress–strain measurements.

*b. Dynamic Modulus*

For measuring complex Young's modulus and internal friction of the samples, the added mass method[4] was used, as described in the previous papers.[1,2] The measurements were performed at a frequency of 200 cycles/sec. at 60% R.H. and 25°C.

*c. Changes in Structure Caused by Heat-Treatment*

**Study by X-Ray Diffraction.** A Geiger counter registration curve of the reflections along the equator for the diffraction pattern of the fiber bundle with CuK$\alpha$ radiation (with the fiber axis perpendicular to the x-ray beam) was made, and the trace of the diffracted intensities for diffraction angles of 7–30° was resolved into amorphous and crystalline peaks, correction being applied for radiation scattered by air and for incoherent scattering (background components due to Compton scattering and thermal agitation) according to the method of Hermans and Weidinger.[5]

The x-ray diffractometer used and the methods of recording the diffraction pattern and of estimating the degree of crystallization were essentially the same as described in the previous paper,[2] except that in the present work, in order to improve the reproducibility of the diffraction pattern obtained, the following conditions were controlled with the utmost care.

(*1*) An exactly constant weight (nearly constant number, about 200) of filaments was always wound parallel and uniformly on a small rectangular wire frame in several layers, the number of layers being chosen so as to keep the irradiated mass of cellulose as constant as possible for the various samples.

(*2*) The width of the slits was made very small (the receiving slit, for instance, being 0.15 mm., i.e.,

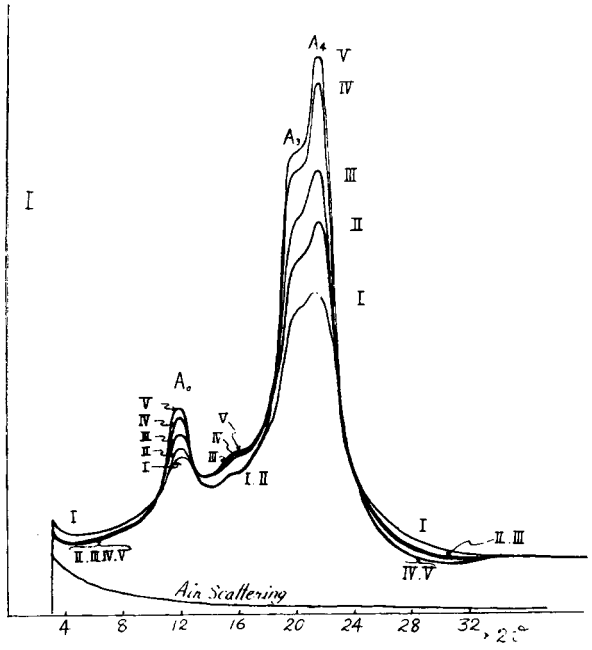


Fig. 1. Geiger counter registration curves of the reflections $A_0$, $A_3$, and $A_4$ of typical samples.

| Specimen no. | Vacuum drying | Preswelling | Heat treatment | Crystallinity, % | Note |
|---|---|---|---|---|---|
| I | 0.5 hr. | Acetic acid (ph = 3.0) | 70°C., 1 hr. | 34.7 | Cf. Table II |
| II | 2 hr. | " | 70°C., 1 hr. | 41.5 (Table II) | " |
| III | 6 hr. | " | 100°C., 1 hr. | 42.3 | " |
| IV | 1 hr. | " | 100°C., 1 hr. | 46.1 | " |
| V | 61% preswelling solution retained | $NH_4OH$ (pH = 9.0) | 70°C., 1 hr. | 47.2 | Cf. Table V |
| Untreated sample | None | None | None | 38.2 | Cf. Tables II, III |

TABLE I
Preparation of Viscose Rayon Fiber Samples for Infrared Spectroscopic Study by the Deuteration Method[a]

| Preswelling bath | Air drying | Vacuum drying (7 mm.) | Deuteration | Heat treatment | Petroleum ether wash and extraction | Air drying | Rehydrogenation in distilled $H_2O$ | Specimen no. Not aged (Fig. 8) | Specimen no. Aged (Fig. 9) |
|---|---|---|---|---|---|---|---|---|---|
| None | None | None | None | None | None | None | None | 1 | 1′ |
| HOAc, pH 3.0 | | | | | | | | | |
| 25°C., 1 hr. | 2 hr. | None | 2 hr. | 70°C., 1 hr. | 25°C., 12 hr. | 2 hr. | 1 hr. | 2 | 2′ |
| " | " | 5–6 hr. | " | " | " | " | " | 3 | 3′ |
| $NH_4OH$, pH 9.0 | | | | | | | | | |
| 25°C., 48 hr. | 2 hr. | None | 2 hr. | None | None | None | 1 hr. | 4 | 4′ |
| " | " | " | " | 70°C., 1 hr. | 25°C., 12 hr. | 2 hr. | " | 5 | 5′ |
| " | " | " | " | 80°C., 1 hr. | " | " | " | 6 | 6′ |
| " | " | " | " | 100°C., 1 hr. | " | " | " | 7 | 7′ |
| " | " | 5–6 hr. | " | 70°C. | " | " | " | 8 | 8′ |
| " | " | " | " | 100°C. | " | " | " | 9 | 9′ |

[a] Viscose film (20 $\mu$ thick) previously extracted with ethanol–benzene mixture (25°C., 48 hr.), washed with distilled $H_2O$, and air-dried for 2–3 hr.

about one-third of that used in the previous experiment[2]).

(*3*) The scanning speed of the goniometer was reduced to about one-fourth that used in the previous experiment[2] so that the reproducibility of the pattern was greatly improved.

In Figure 1 are shown the Geiger Counter registration curves thus obtained for the $A_0$, $A_3$, and $A_4$ reflections of some typical rayon samples.

**Study by Infrared Spectroscopy.** Similarly as described in the previous paper,[2] a qualitative study was made of the change caused by the heat treatment by means of infrared spectroscopy according to the deuteration method of Mann and Marrinan.[6]

For convenience in the spectroscopic investigation, a viscose film instead of rayon fiber was used also in the present work.

The samples taken were as given in Table I.

The deuteration was carried out in the vapor phase in a cell described in the previous paper[2] and the same Perkin-Elmer 112 spectrometer with a LiF prism was used.

## RESULTS AND DISCUSSION

### 1. Effect of Desiccation of the Preswollen Samples

#### *a. Acid-Bath-Treated Fibers*

A series of samples of various degrees of desiccation was obtained by varying the period of vacuum drying (7–8 mm. Hg) of the fibers after preswelling in the acetic acid bath (pH = 3.0). Each of the samples was heat-treated at 70°C. and at 100°C. Results with respect to degree of crystallinity are shown in Table II.

TABLE II
Degree of Crystallinity Estimated by X-Ray Method in Relation to Drying Time of Fibers Preswollen in Acetic Acid Bath (pH = 3.0)

| Vacuum drying time, hr. | Degree of crystallinity, %, of various samples: Untreated | Heated at 70°C., 1 hr. | Heated at 100°C., 1 hr. |
|---|---|---|---|
| 0.5 | | 34.7 | — |
| 1 | | 36.4 | 46.1 |
| 2 | 38.2 | 41.5 | 45.2 |
| 4 | | 36.7 | 44.0 |
| 6 | | 37.2 | 42.3 |

#### *b. Alkaline Bath-Treated Fibers*

Also for fibers preswollen in ammonium hydroxide bath (pH = 10.0, 25°C.), a similar series of various degrees of desiccation was obtained. However in this case, the fibers, after being taken out of solution and squeezed on filter paper to remove the solution mechanically retained by fibers, were each air-dried for different lengths of time, and from the weight increase of fibers thus obtained the amount of solution adsorbed by samples was determined. Results of heat treatment (70°C., 1 hr.) of these samples are given in Table III.

TABLE III
Degree of Crystallinity of Fibers Obtained by Heat Treating Viscose Rayon Preswollen in Ammonium Hydroxide Bath (pH = 10.0) in Relation to the Amount of Solution Retained in the Preswollen Fibers

| Amt. of $NH_4OH$ adsorbed, % | Degree of crystallinity, %, of various samples | |
|---|---|---|
| | Untreated sample | Heated at 70°C., 1 hr. |
| 0 | | 38.6 |
| 47 | | 44.4 |
| 61 | 38.2 | 44.2 |
| 115 | | 39.9 |

The pH ranges employed in the above two experiments, that is, 3.0 for acetic acid bath and 10.0 for the ammonium hydroxide bath, correspond respectively to the maximum swelling of regenerated cellulose, where, according to our experimental results described in the previous paper and given below, typical effects of the heat treatment stabilizing viscose rayon are expected to make their most prominent appearance.

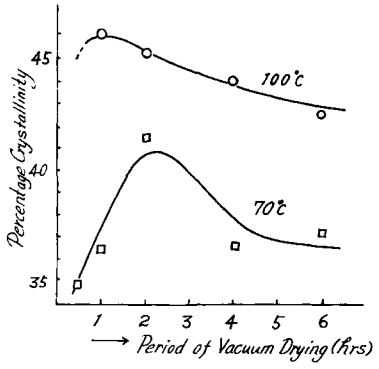


Fig. 2. Degree of crystallinity of the fibers obtained by heat treating (70 and 100°C., 1 hr.) viscose rayon preswollen in an acetic acid bath (pH = 3.0) vs. the duration of vacuum drying of the preswollen fibers.

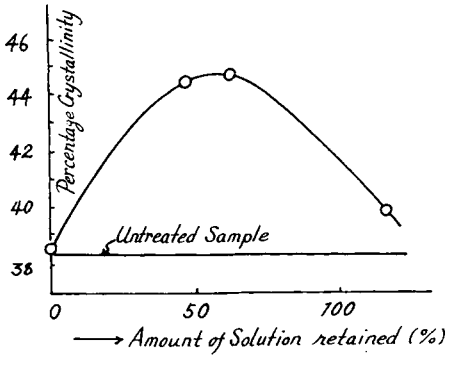


Fig. 3. Degree of crystallinity of the fibers obtained by heat treating (70°C., 1 hr.), viscose rayon preswollen in an ammonium hydroxide bath (pH = 10.0) vs. the amount of the solution retained in the preswollen fibers.

However, as shown by the data in Tables II and III as well as in Figures 2 and 3, the degree of desiccation of the preswollen samples is also involved in some measure in the stabilization and an optimal degree of desiccation seems to be obtained in either of the samples from the two baths given above.

It is natural to expect that at some extreme degree of desiccation the preswollen structure may be in part or wholly deswollen, and consequently the segmental rearrangement to an ordered state may be made more difficult; this may result a decrease in the stabilizing effects of heat treatment.

It may be also possible that at an extremely large moisture content the free water molecules in the micellar interstices may disturb to some extent the segmental motion for this rearrangement.

This may explain the maxima obtained in the percentage crystallinity–drying time curves.

## 2. Dynamic Modulus and Breaking Strength in Relation to the Conditions of Pretreatment of Fibers

Taking account of the optimal degree of desiccation described above, the preswollen samples were thereafter dried to such an extent that the amount of water adsorbed by samples (weight increase) was about 60%.

The data obtained are given in Table IV and shown graphically in Figures 4–5.

From the general trends of the curves, the following conclusions were reached.

(*1*) In the temperature range from room temperature up to 160°C., the dynamic modulus $E'$ shows its maximum in the pH range around 9.0. This is in the pH range where regenerated cellulose shows its maximal degree of swelling[7] (see Fig. 6).

(*2*) Also in the pH range of 7.0–10.0 the $E'$ attain their maxima at the temperature of about 70–90°C., although the $E'$ values do not tend to decrease markedly at higher temperatures (90–160 C.) as is the case when acetic acid is used as the swelling agent and as opposed to the case when sulfuric acid is used as the swelling agent, as has been shown in the previous papers.[1,2]

In spite of the slight lowering of the modulus, the breaking strength decreases quite markedly

TABLE IV
Dynamic Modulus and Breaking Properties in Relation to the Conditions of Pretreatment of Viscose Rayon Fibers

| Heat treatment | pH of $NH_4OH$ bath | Dynamic modulus $E' \times 10^{-11}$, dynes/cm.$^2$ | Breaking strength $f_{max}$, g./den. | Breaking elongation $El_{max}$, % |
|---|---|---|---|---|
| None | | 2.1 | 1.7 | 16 |
| 70°C. | 7 | $2.1_5$ | $2.3_8$ | 19 |
| | 8 | $2.5_0$ | $2.4_0$ | 18 |
| | 9 | $2.9_2$ | $2.9_0$ | 19 |
| | 10 | $2.3_5$ | $1.9_0$ | 14 |
| 85°C. | 7 | $2.2_5$ | $2.3_1$ | 16 |
| | 8 | $2.4_1$ | $2.2_9$ | 19 |
| | 9 | $2.9_3$ | $2.7_5$ | 19 |
| | 10 | $2.4_0$ | $2.0_6$ | 13 |
| 100°C. | 7 | $2.6_0$ | $2.1_6$ | 16 |
| | 8 | $2.4_5$ | $2.3_1$ | 18 |
| | 9 | $2.7_0$ | $2.8_0$ | 18 |
| | 10 | $2.3_2$ | $1.8_5$ | 12 |
| 130°C. | 7 | $2.2_5$ | $2.0_7$ | 16 |
| | 8 | $2.1_5$ | $2.0_0$ | 15 |
| | 9 | $2.6_3$ | $2.6_5$ | 15 |
| | 10 | $2.0_2$ | $1.8_5$ | 13 |
| 160°C. | 7 | $2.2_2$ | $1.9_0$ | 15 |
| | 8 | $2.0_0$ | $1.6_0$ | 13 |
| | 9 | $2.4_2$ | $2.2_0$ | 14 |
| | 10 | $1.9_0$ | $1.5_2$ | 12 |

as the temperature of heat treatment increases beyond 80°C., but this is not so marked as in the case when acid baths (both acetic and sulfuric acid) are used.

Such trends can also be seen in the corresponding crystallinity curves given below. This may indicate that the destructive action of the more volatile acetic acid or ammonium hydroxide toward cellulose at comparable condition is less drastic than that with the less volatile sulfuric acid as swelling agent.

### 3. Degree of Crystallinity and its Relation to the Conditions of Pretreatment of Fibers

The data obtained on the degree of crystallinity as estimated from the results of x-ray measurements, are given in Table V and shown graphically in Figure 7.

The general trends of the curves indicating the effects of pH and temperature of the heat treatment are similar to those of the curves regarding dynamic modulus in the following respects.

(*1*) In the temperature range from room temperature up to 160°C., the crystallinity reaches a

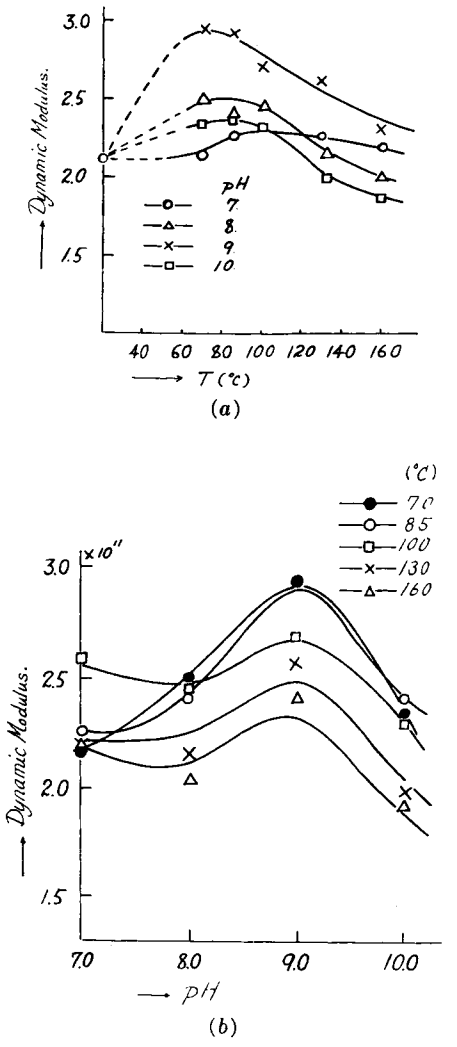


Fig. 4. Dynamic modulus of the fibers obtained by heating viscose rayon pretreated in ammonium hydroxide baths of various concentrations at various temperatures: (*a*) $E'$ vs. temperature; (*b*) $E'$ vs. pH.

maximum in the pH range of about 9.0, i.e., in the range where maximum swelling of regenerated cellulose is shown in the alkaline pH region (see Fig. 6).

(*2*) In the pH range 7.0–10.0 the crystallinity–temperature curves attain a maximum at a temperature of about 70–100°C., although the crystallinity does not tend to decrease so markedly at higher temperatures as in the case with the less volatile sulfuric acid solution as the swelling agent.[1]

What is most remarkable is the fact that the stabilizing effects of heat treatment as exhibited by the dynamic modulus, breaking strength, and crystallinity of viscose rayon at the optimal

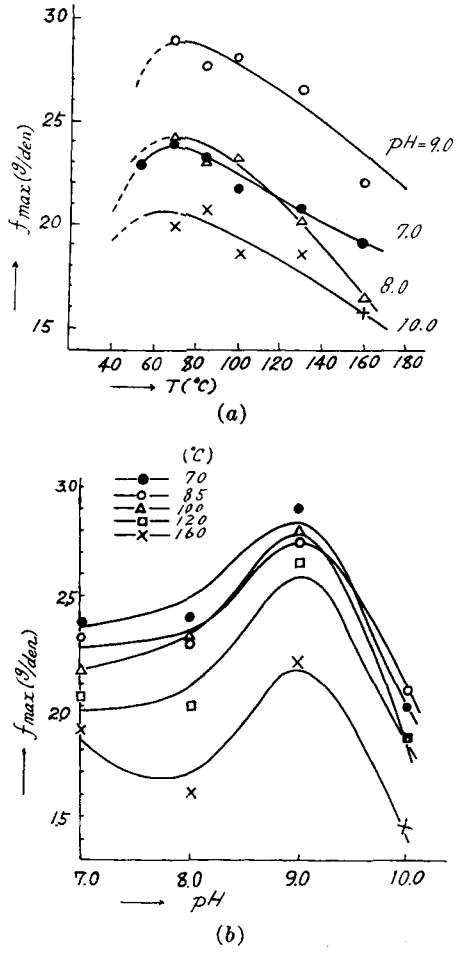


Fig. 5. Breaking strength $f_{max}$ of fibers obtained by heating viscose rayon pretreated in ammonium hydroxide baths of various concentrations at various temperatures: (*a*) $f_{max}$ vs. temperature; (*b*) $f_{max}$ vs. pH.

condition of pretreatment (i.e., at the pH optimal for maximal hydration of regenerated cellulose, pH = 9.0 for the ammoniacal bath and heat treatment temperatures just above the glass transition point) are much larger than those obtained by heat

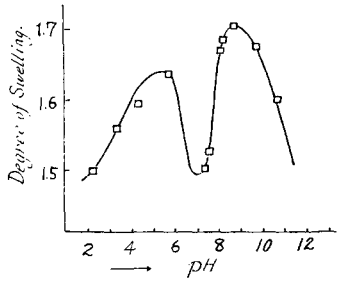


Fig. 6. Plot of degree of swelling of regenerated cellulose (viscose film) vs. pH of the solution at the swelling equilibrium.

TABLE V
Degree of Crystallinity in Relation to Condition of Pretreatment of Viscose Rayon Fibers of Ammoniacal Preswelling Baths

| Heat treatment temperature, °C. | Crystallinity, %, of samples swollen in various $NH_4OH$ baths | | | | |
|---|---|---|---|---|---|
| | pH 7 | pH 8 | pH 9 | pH 10 | pH 11 |
| 70 | 39.3 | 44.2 | 47.2 | 46.7 | — |
| 85 | 42.6 | 48.0 | 46.8 | 45.2 | — |
| 100 | 45.2 | 46.2 | 46.2 | 44.6 | — |
| 130 | 43.4 | 43.3 | 46.2 | 46.2 | 45.2 |
| 160 | 41.6 | — | 46.8 | 44.1 | 42.1 |

treatment of acid bath-preswollen fibers. For instance, the increase in crystallinity and in breaking strength on heat treatment of fibers preswollen in the ammoniacal bath at pH = 9.0 and heat-treated at 70–85°C. is as large as 9% and 70%, respectively, over that of the untreated sample while the corresponding increases in the case of acid-bath-treated fibers amount only to about 3% and

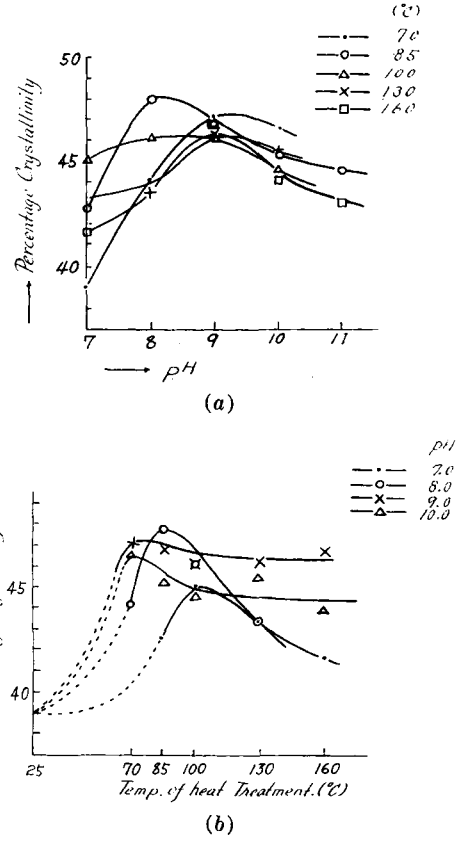


Fig. 7. Variation of degree of crystallinity with the conditions of pretreatment of fibers by means of ammoniacal preswelling baths: (*a*) crystallinity vs. temperature; (*b*) crystallinity vs. pH.

30% with sulfuric acid as the swelling agent,[1] and respectively, $\Delta f_{max}$ being about 42% in the case of acetic acid.

This marked effect with ammoniacal solution as the preswelling agent for heat treatment of fibers is also clearly indicated by the results of infrared spectroscopy, as shown below.

### 4. Results of Infrared Spectroscopy

The spectra obtained were indicated as the optical density–frequency curves as shown in Figure 8 where optical density means logarithm of the transmission ratio of an NaCl plate to that of the film specimens. Of the specimens described in Table I, the spectroscopic measurements given in Figure 8 were all carried out in one to two days after the preparation of the films.

As it seems to be of some significance to consider the aging effect, the same samples for which results are given in Figure 8 were left in air for about three months before being subjected to a second spectroscopic measurement. The results, given in Figure 9, were considered in comparison with those given in Figure 8.

**Effect of the Temperature of Heat Treatment.** As seen from the spectra shown in Figures 8 and 9, the samples heat-treated after being deuterated show, in general, after rehydrogenation, bands characteristic of the OD-groups in the crystalline regions which have not been rehydrogenated, that is, the band due to the so-called "resistant" OD groups. Moreover, these "crystalline" peaks appear more markedly as the temperature of heat treatment rises. This is clearly indicated by the

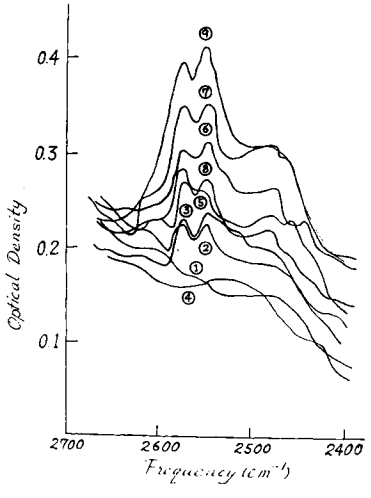


Fig. 8. Infrared spectra in the region of absorption by OD-groups at 2700–2400 cm.$^{-1}$ of viscose films given under various pretreatments (non-aged specimens) (see Table I).

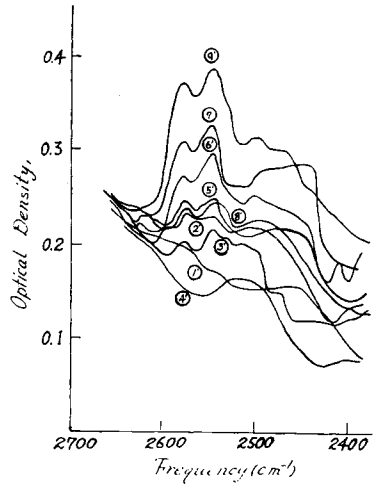


Fig. 9. Specimens of Fig. 8 after aging for 3 months (see Table I).

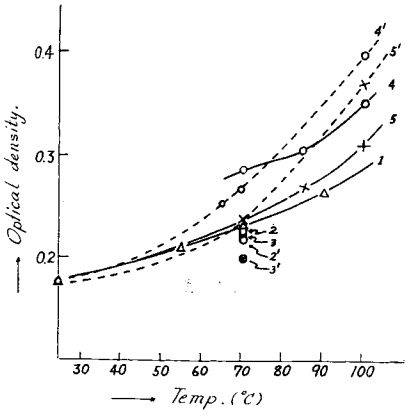


Fig. 10. Plot of optical density at 2580 cm.$^{-1}$ vs. heating temperature: (*1*) preswollen in $H_2SO_4$, air-dried; (*2*) preswollen in HOAc, air-dried; (*2'*) preswollen in HOAc, vacuum-dried; (*3*) preswollen in HOAc, air-dried, aged; (*3'*) preswollen in HOAc, vacuum-dried, aged; (*4*) preswollen in $NH_4OH$, air-dried; (*4'*) preswollen in $NH_4OH$, vacuum-dried; (*5*) preswollen in $NH_4OH$, air-dried; aged; (*5'*) preswollen in $NH_4OH$, vacuum-dried, aged.

curves in Figure 10 as well as in Figure 11, in which the optical density of the typical absorption band is plotted against the temperature of the heat treatment for each of the specimen series.

The formation of these crystalline peaks, that is, the resistant OD-groups, is plausibly ascribed to the crystallization effect caused by the deuterated amorphous regions.[6] The spectroscopic results given in Figures 10 and 11 show that this crystallization effect on heat treatment of the preswollen fibers becomes apparent at about 70°C. and, moreover, becomes gradually more marked as temperature rises. While there is not a sudden appearance of this effect just at 70°C. is evident,

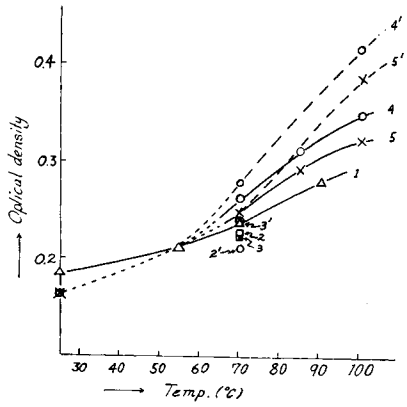


Fig. 11. Plot of optical density at 2548 cm.$^{-1}$ vs. heating temperature. Legend as for Fig. 10.

around that temperature the most typical effects of the heat treatment for stabilizing regenerated cellulose, as shown by the various physical and mechanical properties also make their most prominent appearance. This has been also referred to the previous paper,[2] with respect to the results of heat treatment of rayon fibers preswollen in acid baths.

**Aging Effect.** As shown in Figures 10 and 11, throughout the higher temperature range (70–100°C.) where a strong crystallization effect is to be expected, the intensity of the "crystalline" absorption bands characteristic of OD-groups is distinctively reduced by aging the rehydrogenated rayon fibers.

This would seem to indicate that at least a part of the crystalline structure of the regenerated cellulose made of such OD-groups is not in reality sufficiently stable, and that these OD-groups are partly rehydrogenated by atmospheric moisture during the aging while the resistant OD-groups, in the real sense of meaning, remain.

**Effect of Desiccation of the Preswollen Samples.** From the results of the x-ray study, it was shown above that there is a degree of desiccation of the preswollen fibers optimal for effecting their stabilization by the heat treatment. However, from the results of infrared spectroscopy as shown in Figures 10 and 11, such an indication is not so apparent. The vacuum-dried samples show in general, contrary to our expectation, rather higher "crystalline" peaks than the air-dried samples, especially at higher temperatures (85–100°C.). (Compare in Figs. 10 and 11 specimens 8 and 9 and 8′ and 9′ with the corresponding specimens 5–7 and 5′–7′, respectively.)

It may be possible that, in effecting the crystallization of the OD-cellulose molecules by the heat treatment, the presence of $H_2O$ molecules in the fibrous medium (naturally expected in the case of unsufficiently dried specimens may exert some disturbing effect so that the relaxation of frozen-in structure caused by the preswelling, which is supposed to be effective in causing the crystallization through the heat treatment, may be handicapped or wholly nullified.

Moreover, it is also possible that the amorphous structure, which may be closely packed as a result of the strong desiccation relaxes during the vapor-phase deuteration which is carried out within a few hours after desiccation of the preswollen fiber.

However, it is of interest to point out that, although at higher temperatures (85–100°C.) the effect of desiccation does not go along with our expectation, at a lower temperature (around 70°C.) a slight indication of such a trend is apparent, especially from the characteristic absorption band at 2580 cm.$^{-1}$ (compare 8 or 8′ with 5 or 5′ and 3 or 3′ with 2 or 2′). However, our present experimental knowledge does not permit any definite answer as yet.

To permit the results of infrared spectroscopy to be compared with those of x-ray studies, the degree of crystallinity must be estimated also from the intensity of the characteristic absorption bands, the intensity of the completely amorphous OD-hydrate cellulose at the corresponding frequency being taken as the standard. More precise experimental investigations and more quantitative treatments of this problem are now being carried on in our laboratory and will be reported in future papers.

**Comparison of Ammoniacal and Acid Baths for Preswelling Sample for Heat Treatment.** The results of dynamic modulus, breaking strength, and of the crystallinity estimates from x-ray studies indicate that the effects of heat treatment for stabilizing viscose rayon, as exhibited by these properties at the optimal conditions for its pretreatment, are much larger when an ammoniacal bath (pH = 9.0) is used than when compared when an acid (sulfuric or acetic) bath (pH = 3.0) is used as the preswelling agent. Such a trend is seen clearly also from the results of infrared spectroscopy (Figs. 10 and 11), where the plots of optical density-versus temperature of heat treatment when ammonium hydroxide bath (pH = 9.0) is used as the preswelling medium and those where sulfuric or acetic acid baths (pH = 3.0) are used, are compared. The effectiveness of the ammonium hydroxide bath is clearly indicated throughout the range of higher temperatures (70–100°C.) where the effects of the heat treatment in stabilizing viscose rayon, as exhibited by mechanical properties, are most marked.

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## Synopsis

In continuation of a previously reported experimental study on stabilizing viscose rayon by heat treatment, in which acid baths were used as the preswelling agents for heat treatment of regenerated cellulose further experiments were performed in which ammonium hydroxide solutions served as the preswelling agent. From the effects of heat treatment of the fibers preswollen in ammonium hydroxide bath, as exhibited by dynamic modulus, breaking strength, degree of crystallinity (estimated from x-ray data), etc., it was confirmed again that, when viscose rayon preswollen in an ammonium hydroxide bath of the concentration or the pH range optimal for it maximal hydration (pH = 9.0) is heat treated at the temperature just above the glass transition temperature of regenerated cellulose (ca. 70–90°C.), the effects of the heat treatment in stabilizing viscose rayon are most marked. Moreover the effects of heat treatment, as exhibited by these properties of rayon at the optimal condition are much larger in this case than when the heat-treated fibers are preswollen in an acid bath. This effect is also clearly indicated by the results of infrared spectroscopy studies according to the deuteration method. With the use of a series of fiber samples preswollen in acetic acid as well as ammonium hydroxide bath and dried at various degrees of desiccation results were obtained which indicate that there is an optimal degree of desiccation for effecting maximal stabilization.

## Résumé

À la suite d'une étude expérimentale publiée précédemment, dans laquelle des solutions acides ont été employées comme agent prégonflant de cellulose régénérée en vue de son traitement thermique, nous avons poursuivi des expériences plus poussées avec des solutions d'hydroxyde d'ammonium comme agent prégonflant. Les effets du traitement thermique sur les fibres prégonflées dans un bain d'hydroxyde d'ammonium sont mesurables par le module dynamique, la résistance à la rupture et le degré de cristallinité (estimé aux rayons-X); ils confirment l'effet, qui a été observé déjà avec des fibres traitées dans un bain acide: en chauffant les fibres de viscose prégonflées dans un bain d'hydroxyde d'ammonium (le pH 9.0 étant la condition optimum d'hydratation), à une température juste au dessus de celle de la transition vitreuse de la cellulose régénérée (c'est à dire 70–90°C environ), on obtient les meilleurs effets du traitement thermique pour stabiliser les fibres viscoses. Cet effet excellent de la solution d'ammoniaque (pH = 9.0) comme agent prégonflant des fibres pour le traitement thermique a été prouvé également par des études spectroscopiques à la lumière infra-rouge. On a utilisé une série d'échantillons de fibres de divers degrés de dessication et prégonflés dans un bain d'acide acétique ou d'hydroxyde d'ammonium, les résultats expérimentaux obtenus indiquent pour chaque libre prégonflée l'existence d'un degré de dessication optimum pour l'obtention d'une stabilité maximale.

## Zusammenfassung

In Fortsetzung der früher von uns veröffentlichten experimentellen Untersuchungen über die Stabilisierung von Viscoseseidenfasern durch Wärmebehandlung, bei welchen als Vorquellungsmittel für die Regeneratcellulose vor der Wärmebehandlung wässrige Lösungen von Säuren (Schwefelsäure- und Essigsäurelösungen) verwendet worden waren, wurden weitere Versuche mit sehr verdünnten wässrigen Lösungen von Ammoniumhydroxyd verschiedener Konzentration als Vorquellungsmittel durchgeführt. Der Effekt dieser Wärmebehandlung wurde wie früher durch Messung des dynamischen Elastizitätsmodul, der Bruchfestigkeit, des Betrages des kristallinen Anteils (geschätzt nach der Methode von Hermans und Weidinger) usw. ermittelt. Es wurde wieder die von uns früher bei Anwendung von Säurebädern beobachtete experimentelle Tatsache bestätigt, dass bei Viscoseseidenfasern dann bei Wärmebehandlung in dem der Einfriertemperatur der Regeneratcellulose benachbarten Temperaturbereich von 70–90°C die Stabilisierung der Fasern durch diese Behandlung am stärksten ist, wenn sie vorher in einem Ammoniumhydroxyd-Bad (pH = 9.0), dessen Konzentration oder pH dem Quellungsmaximum der Fasern entspricht, gequollen worden sind. Ausserdem wurde gezeigt, dass die Stabilisierungswirkung der Wärmebehandlung an den im Ammoniumhydroxyd-Bad bei optimalen Bedingungen der Vorbehandlung vorbehandelten Fasern, wie die obengenannten mechanischen und physikalischen Eigenschaften erkennen lassen, viel stärker ist als im entsprechenden Falle der Wärmebehandlung von Fasern, die im Säure-Bad vorgequollen wurden. Diese besondere Wirkung der ammoniakalischen Lösung (pH = 9,0) konnte auch durch die Ergebnisse der qualitativen Ultrarotuntersuchung nach der Deuterierungsmethode von Mann und Marrinan deutlich gezeigt werden. Bei Verwendung einer Reihe von Proben verschiedenen Trocknungsgrades wurden an Fasern, die im Essigsäure-Bad oder im Ammoniumhydroxyd-Bad vorgequollen worden waren, Resultate erhalten, welche dafür sprechen, dass es für jede der vorgequllenen Fasern einen optimalen Trocknungsgrad gibt, der den stärksten Stabilisierungseffekt liefert.

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