

## X-RAY STUDIES OF CRYSTALLITE ORIENTATION IN CELLULOSE FIBERS. III

FIBER STRUCTURES FROM COAGULATED CELLULOSE<sup>1</sup>

WAYNE A. SISSON

*Boyce Thompson Institute for Plant Research, Inc., Yonkers, New York**Received August 30, 1939*

It is well known that crystallite orientation may be closely correlated with the physical, chemical, and optical properties of cellulose fibers. The laws which govern the production of crystallite orientation in synthetic fibers, therefore, are not only of theoretical interest but also of practical importance. For example, the tensile strength and elongation of rayon fibers may change several hundred per cent as the orientation is varied from a random to a parallel orientation. The usual method of increasing orientation in rayons is by stretching. This produces an alignment of the major (*b*) axes of the cellulose crystallites parallel to the direction of stretching. The cellulose crystallite also possesses a secondary or minor orienting tendency, as shown by the fact that a minor axis [101] of the crystallite is oriented parallel to the direction of shrinkage when swollen cellulose is dehydrated (3).

It is the purpose of the present paper to extend the previous investigations on the orientation behavior of the native cellulose crystallite (2, 3) to that of the hydrate cellulose crystallite which exists in fibers produced from coagulated cellulose, to study separately and collectively the factors which affect the production of orientation, and to formulate into a rule the general orientation behavior of cellulose. The paper is divided into four parts: (*a*) the effect of shrinkage produced by dehydration, (*b*) the effect of mechanical deformation, (*c*) discussion of the combined effects of shrinkage and deformation in producing the various types of orientation, and (*d*) citation of the orientation found in Cellophane and rayons as an application of the above factors.

## MATERIALS AND METHODS

The majority of samples examined were prepared either from alcohol-benzene-extracted and Kiered cotton or from commercial wood pulp which was dispersed and coagulated from viscose solutions as recommended by Snell (5). The general orientation behavior was also checked

<sup>1</sup> Presented before the Division of Cellulose Chemistry at the Ninety-third Meeting of the American Chemical Society, held at Chapel Hill, North Carolina, April 12-15, 1937. This paper is a contribution from the Cellulose Department of the Chemical Foundation, located at the Boyce Thompson Institute for Plant Research, Inc., Yonkers, New York.

on cellulose coagulated from cuprammonium, quaternary ammonium hydroxide, and phosphoric acid, and also on cellulose regenerated from the acetate and nitrate derivatives. After subjecting the hydrate cellulose thus formed to various restricted conditions during drying, the final dried samples were examined with x-rays as described in the earlier publications (2, 3, 4). The Cellophane and rayon samples examined were of the usual commercial variety.

Since the present investigation represents a large number of individual experiments performed under varying conditions over a period of several years, space does not permit a detailed description of each; only a few experiments are described and a summary of the results is given. The terms for the various types of orientation (random, uniplanar, selective uniplanar, uniaxial, and biaxial) are used as defined in the earlier paper (3). Instead of representing the results with stereographic projections, however, they are illustrated by drawings of the unit cell (figure 1A). The orientation of the unit cell is located by the  $b$ -axis (direction of cellulose chain)

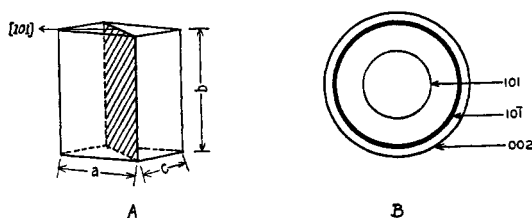


FIG. 1. Schematic representation of unit cell (A) and x-ray diagram (B) of hydrate cellulose (see text for explanation).

lose chain) and the 101 plane which is shaded in the drawing. The minor axis [101] is perpendicular to the 101 plane. The x-ray diagram of hydrate or mercerized cellulose is represented in figure 1B. The concentric rings of increasing diameter in the diagram are the 101,  $10\bar{1}$ , and 002 diffraction lines, respectively.

#### SHRINKAGE

Coagulated cellulose, when first formed, is usually in a highly swollen condition. The present observations would indicate that the equilibrium condition of a swollen sample is random orientation. Upon dehydration, produced either by chemical reagents, or by drying, considerable shrinkage in volume takes place, and, simultaneously with this shrinkage, orientation is produced. The type of orientation is apparently governed by the direction of shrinkage, and the degree of orientation by the degree or percentage of that shrinkage. The x-ray results on shrinkage are summarized in figure 2.

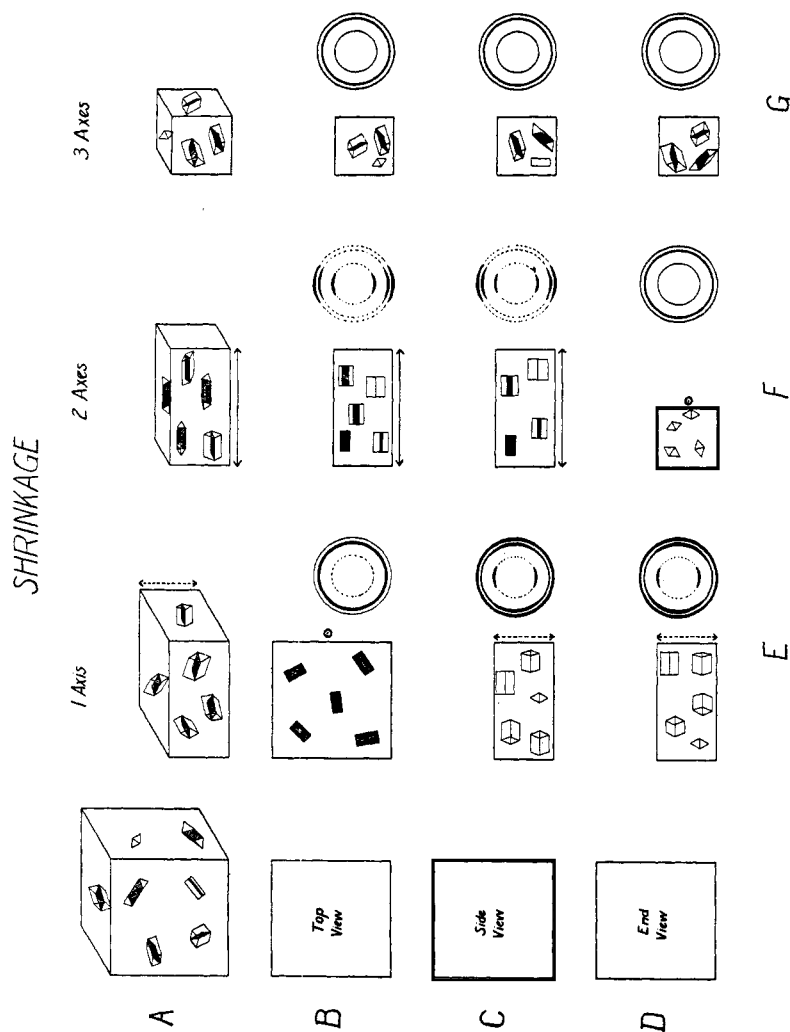


Fig. 2. Schematic representation of type of orientation and corresponding x-ray diagrams obtained when swollen hydrate cellulose shrinks along various axes (see text for explanation).

In figure 2A, a cube of swollen coagulated cellulose having random orientation is diagrammatically represented in the upper left-hand corner. The types of orientation obtained when the cube shrinks along different axes are represented diagrammatically in the vertical columns E, F, and G. The corresponding x-ray diagrams are shown with the sketches. The horizontal columns A, B, C, and D show the orientation and x-ray diagrams when viewed from different positions. Arrows indicate the direction of fiber axes; solid lines represent major axes (orientation of  $b$ -axes of unit cell), while dotted lines represent minor axes (orientation of perpendiculars to 101 plane of unit cell). Thus, figure 2BE refers to the orientation produced by shrinkage in one direction when viewed from the top (axis of shrinkage).

If the cube shrinks along one axis (figure 2AE), the 101 planes are oriented perpendicular to the direction of shrinkage, but there is random arrangement of the  $b$ -axes about this direction. When viewed from the top (figure 2BE), the 101 planes are parallel to the top surface.<sup>2</sup> Since diffraction is possible from the 101 planes only when they form an angle of  $6^\circ$  with the x-ray beam, these planes are not in a diffracting position, hence the 101 line is absent in the diffraction pattern. The  $10\bar{1}$  planes, which form an angle of slightly less than  $90^\circ$  to the 101, are in a diffracting position and an intense  $10\bar{1}$  line is present showing random orientation. When viewed from the side (figure 2CE) the 101 planes, being parallel to the top surface, are now in a diffracting position, as evidenced by two meridian reflections in the x-ray diagram (minor fiber axis parallel to shrinkage axis). The  $10\bar{1}$  and 002 planes diffract only when the unit cells are approximately end-on. Since the  $10\bar{1}$  and 101 planes intersect at an angle of less than  $90^\circ$ , the  $10\bar{1}$  planes thus diffract near the equator in four positions which merge to form two equatorial arcs. The 002 planes behave in a similar manner, with the exception that the 002 arcs are much broader. The end view (figure 2DE) is the same as the side. As in the previous paper (3), the type of orientation resulting from shrinkage along one axis will be referred to as a selective uniplanar orientation, because the only limitation imposed is that the 101 planes be oriented parallel to a plane (surface) which is perpendicular to the direction of shrinkage.

If shrinkage takes place in two directions<sup>3</sup> (figure 2AF), the  $b$ -axes of the unit cells are oriented parallel to the axis which did not shrink, but the unit cells have random orientation around their  $b$ -axes. When viewed from the

<sup>2</sup> In drawing the x-ray diagrams the x-ray beam is assumed to pass through the sample in the same relative position as the direction of view. The diagrams are drawn with a considerable deviation from the preferred type, since a large deviation was found in all of the experimentally prepared samples.

<sup>3</sup> In referring to shrinkage along two axes it is implied that shrinkage also takes place at all angles in a plane containing these two axes, which are located at  $90^\circ$  to each other.

top (figure 2BF), the 101,  $10\bar{1}$ , and 002 planes all diffract, giving equatorial reflections (fiber axis parallel to direction which did not shrink). The same orientation is present when viewed from the side (figure 2CF). When viewed from the end (figure 2DF), the direction is parallel to the  $b$ -axes of the unit cells (fiber axis), and the 101,  $10\bar{1}$ , and 002 planes all diffract, showing a random orientation. This type of orientation resulting from shrinkage along two axes will be referred to as a uniaxial orientation, because the only limitation imposed is that the  $b$ -axes of the unit cell be oriented parallel to an axis (fiber axis).

If shrinkage takes place in all directions (figure 2AG), the unit cells are oriented in all directions, and there is random orientation when viewed from any direction.

#### DEFORMATION

Another property of swollen coagulated cellulose is that it can be deformed, either by tension or pressure, to produce preferred orientation. Figure 3 summarizes the results obtained by elongation and contraction.

In figure 3 a cube of swollen material, showing random orientation, is represented diagrammatically in the upper left-hand corner. If the cube is elongated along one axis and allowed to contract only along one axis (figure 3AE), then the  $b$ -axes of the unit cells are oriented parallel to the axis of elongation and the 101 planes perpendicular to the axis of shrinkage. When viewed from the top (figure 3BE), the  $b$ -axes are oriented parallel in a horizontal direction (fiber axis), while the 101 planes are parallel to the top surface. As a result, the 101 planes are not in a diffraction position; the  $10\bar{1}$  and 002 planes, however, do diffract, each giving two equatorial reflections. When viewed from the side (figure 3CE), the 101 planes diffract, giving two equatorial reflections, while the  $10\bar{1}$  planes are not in a diffracting position. When viewed from the end (figure 3DE), the 101 planes diffract at the meridian (minor axis); the  $10\bar{1}$  planes diffract at the equator, and the 002 diffract in four positions, two of which merge with the result that two broad equatorial arcs are formed. This type of orientation, produced by shrinkage on one axis and elongation on one axis, will be referred to as biaxial or selective uniaxial orientation, because the  $b$ -axes of the unit cells are oriented parallel to an axis (major fiber axis) and the 101 planes are oriented parallel to a plane containing the major axis (minor fiber axis perpendicular to plane).

If the cube is elongated along one axis, and contracted along two axes (figure 3AF), then the  $b$ -axes of the unit cell are oriented parallel to the axis of elongation (fiber axis), with the 101 planes rotated at random around the  $b$ -axes. This type of uniaxial orientation is the same as that obtained by shrinkage along two axes (figure 2AF). When viewed from the top (figure 3BF) or side (figure 3CF), all three planes diffract to give

# ELONGATION

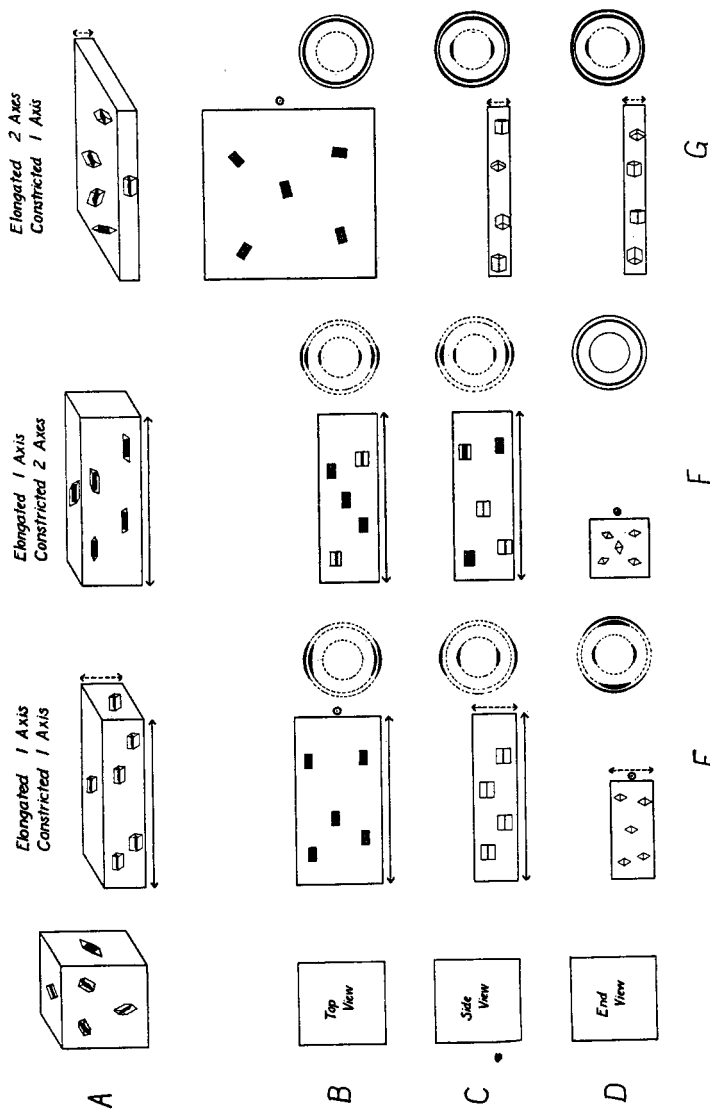


Fig. 3. Schematic representation of type of orientation and corresponding x-ray diagram obtained when swollen hydrate cellulose is deformed along various axes (see text for explanation).

equatorial reflections; when viewed end-on, all planes diffract to give a random orientation.

If the cube is elongated in two directions and contracted along a third axis (figure 3AG), the same type of selective uniplanar orientation is obtained as when shrinkage occurs along one axis (figure 2AE); the 101 planes are oriented perpendicular to the axis of contraction with the *b*-axes oriented at random in a plane perpendicular to the axis of contraction.

#### DISCUSSION

The results obtained by either shrinkage or elongation are summarized in figure 4. A random orientation is obtained in the swollen condition or by shrinkage (S) along three axes; uniaxial orientation by shrinkage along two axes, or by elongation (E) on one axis and shrinkage along two; uniplanar orientation by shrinkage along one axis, or by elongation on two axes and shrinkage along one; and biaxial orientation by shrinkage along one axis and elongation along one axis.

It is difficult to evaluate separately the effect of shrinkage and deformation, since the two always act collectively in producing a dry sample necessary for x-ray diffraction analysis. The most tangible factor which may be correlated with the production of orientation appears to be the relative change in sample dimensions. In terms of dimensional changes, the following general conclusion may be drawn: Whenever there is a relative increase in dimension of a sample in one direction, the *b*-axes of the unit cell tend to orient parallel to that direction; if there is a relative decrease in dimension in one direction, the 101 planes are oriented perpendicular to that direction. The degree of orientation in each case is proportional to the relative change in dimensions of the sample. If one cares to think in terms of the cellulose chain instead of the unit cell, the cellulose chain tends to orient parallel to the direction of increase, while the hydroxyl groups of the glucose unit tend to rotate in the direction of decrease.

All four types of orientation have been produced experimentally: random orientation by permitting a sample to dry while supported on a blotter or mercury; uniaxial by stretching a fiber or allowing it to dry with ends fixed; uniplanar by pressing or allowing a film to dry on a glass plate so that it shrinks only in thickness; and biaxial by rolling or pressing a sample in a groove, so as to elongate along one axis and shrink along one axis. The experimental conditions necessary for the production of these different types of orientation have been given in greater detail in an earlier paper (3). In each sample there is a rather wide deviation from its preferred type of orientation.

After a given type of orientation is formed, it is possible in some instances to change from one type to another. For example, if a uniplanar sample

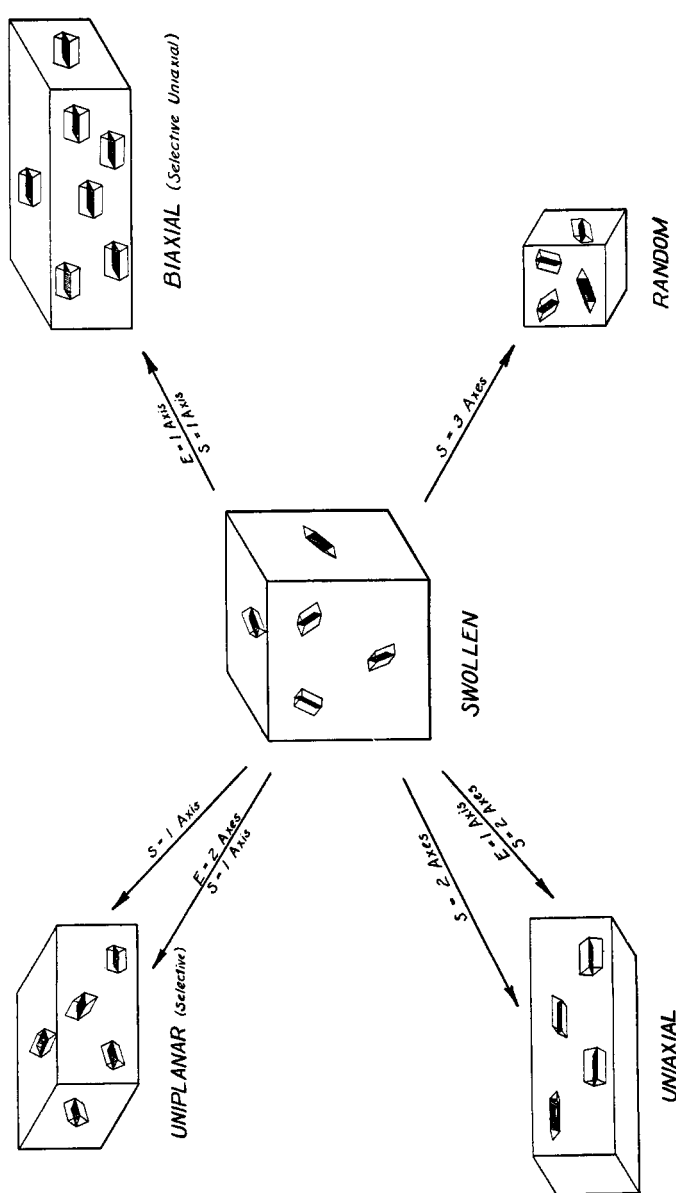


FIG. 4. Schematic representation of various types of orientation and how they may be obtained from swollen cellulose (see text for explanation).



is stretched (perpendicular to fiber axis) it is changed first into an imperfect biaxial and eventually into a uniaxial orientation. If uniaxial or biaxial oriented samples are pressed (perpendicular to fiber axis), they are changed into a uniplanar orientation.

Preliminary results indicate that certain general laws of swelling are closely related to the above general laws of shrinkage and deformation. It is obvious, however, that a distinction must be made between inter- and intra-crystalline swelling or shrinkage. In reswollen samples where only intercrystalline swelling is involved, shrinkage or deformation may not produce the same quantitative effect as in freshly coagulated samples. These and related factors pertaining to the mechanism of cellulose orientation are being investigated further.

#### APPLICATIONS

The present discussion of the orientation found in industrial samples produced from coagulated cellulose will be limited to Cellophane and viscose rayons.

##### *Cellophane*

If the x-ray beam is passed perpendicular to the surface of Cellophane, the 101 line is missing, while the  $10\bar{1}$  and the 002 show a random orientation. With the beam parallel to the plane of the sheet, the 101 line now appears as two strong intensity maxima, and the  $10\bar{1}$  as two weaker intensity maxima at right angles to the 101, while the 002 shows two broad intensity maxima in the same quadrants as the  $10\bar{1}$ . This type of pattern, as previously pointed out, is typical of a selective uniplanar orientation (figure 2AE or 3AG), which may be produced either by shrinkage along one axis or by elongation along two and shrinkage along one. This selective orientation may be anticipated, since the principal shrinkage takes place perpendicular to the sheet in the usual commercial method of producing Cellophane.

In sheets of commercial Cellophane, the above type of orientation is often found in a modified form. For example, the selective orientation of the 101 plane may be less perfect, or there may be a preferred orientation of the *b*-axes in the plane of the sheet. Figure 5A is the x-ray diagram made near the edge of a sheet of Cellophane, with the beam perpendicular to the flat surface. The 101 line is missing, but the  $10\bar{1}$  line does not have a completely random orientation. This condition is typical of a uniplanar orientation with a slight tendency toward a biaxial orientation, and it probably originated during the production of the sheet by an equivalent shrinkage or elongation along an axis lying in the plane of the Cellophane sheet.

The existing type of orientation can be modified also by deformation in

the dry condition. Figure 5B is the x-ray diagram (beam perpendicular to surface) of the same sample as figure 5A after 10 per cent elongation, produced by stretching a strip of the Cellophane. The 101 now appears as a faint arc, and the  $10\bar{1}$  is more sharply oriented,—the orientation is beginning to change to a uniaxial orientation. After 30 per cent elongation (figure 5C), all lines are present as sharp intensity maxima,—the orientation is uniaxial. If the sample is treated with steam and allowed to shrink, the orientation does not completely reverse itself. There is a "hysteresis effect" with the uniaxial orientation tending to be more pronounced on the return curve. By repeating the process of stretching and relaxing, it is possible to change the orientation without the usual corresponding change in dimensions of the sample.

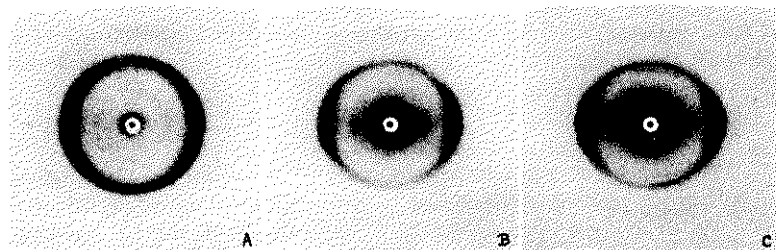


FIG. 5. X-ray diagrams of Cellophane with x-ray beam perpendicular to sheet: A, unstretched; B, stretched 10 per cent; C, after stretching 30 per cent.

### *Rayons*

In the industrial production of rayons, deformation is usually followed by or produced simultaneously with shrinkage; the two factors either reinforce or oppose each other, thus complicating the situation and making it difficult to evaluate the factors which influence the production of orientation. Many workers have assumed that the orientation present in unstretched rayon filaments is produced before coagulation, while the viscose is passing through the spinnerette, and that the rôle of the coagulating agent is primarily to "fix" the orientation already present. Although orientation may be produced in the spinnerette, the present results indicate that the degree and type of shrinkage is the more important factor in producing the final orientation in the dried filament. The composition and length of spinning bath, rate of spinning, and filament diameter all have a pronounced influence, but here, too, the orientation can be correlated to a certain degree with the change in dimensions of the fiber during the coagulating and drying process. In figure 6 there is represented diagrammatically the cross section (figure 6AD), orientation (figure 6BD), and the x-ray diagram (figure 6CD) of a swollen rayon fiber. Al-

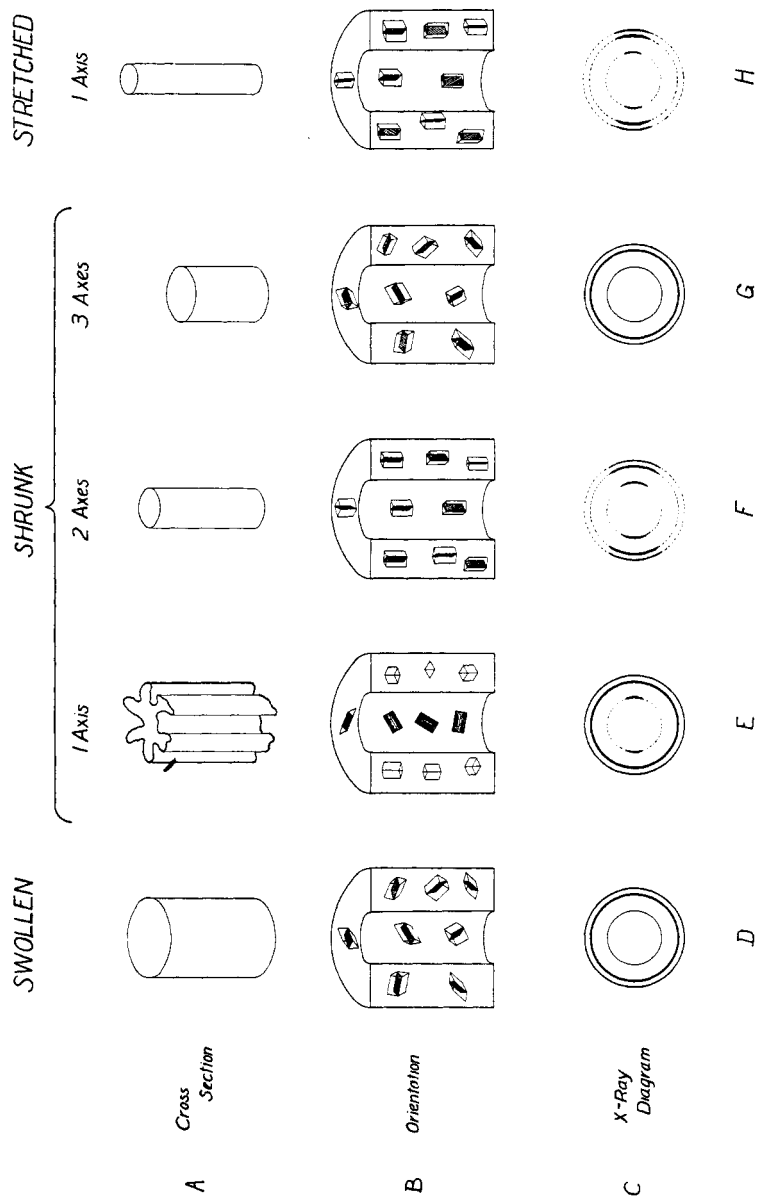


FIG. 6. Schematic representation of cross section, type of orientation, and x-ray diagram obtained when rayon filaments shrink along various axes (see text for explanation).

though shrinkage along one axis<sup>4</sup> could occur either in the longitudinal, tangential, or radial direction, only the latter possibility will be considered. Figure 6AE represents the probable effect of shrinkage only in the radial direction. Since the circumference of the fiber does not change, the cross section could assume any shape between the serrated type (figure 6AE) and a flat ribbon-like type. As pointed out in a previous section, radial shrinkage should produce a selective uniplanar orientation with the 101 planes parallel to the filament surface and the *b*-axes randomly arranged in a plane parallel to the surface. With the x-ray beam perpendicular to the fiber axis, the 101 line should exist as equatorial reflections and the  $10\bar{1}$  as a random orientation (figure 6CE).

In the case of shrinkage along two axes, there are also three possibilities, only one of which is represented,—shrinkage in the radial and tangential direction (figure 6AF). This produces a uniaxial orientation with the *b*-axes parallel to the fiber axis; all three planes diffract as intensity maxima on the equator (figure 6CF).

Shrinkage along three axes (figure 6AB) can occur in only one way to produce a random orientation.

In the case of elongation, there is only one direction in which a rayon fiber can be stretched,—in the direction of the fiber axis, which tends to produce a uniaxial orientation parallel to the fiber axis (figure 6AH). In practice, however, any combination of the seven shrinkage possibilities may have begun to occur or may be in the process of occurring while elongation is taking place, giving a large number of possibilities, the detailed discussion of which space does not permit.

Each type of orientation illustrated in figure 6 has been produced experimentally. Figure 7A is the x-ray diagram of a viscose fiber spun and allowed to dry without tension. All of the diffraction lines show a random orientation. Figure 7B is a fiber spun under the same conditions, with the exception that the ends of the fiber were fastened to a support immediately after coagulation so that longitudinal shrinkage was prohibited. The 101 diffraction line shows some orientation, while the  $10\bar{1}$  and 002 have a random orientation. In figure 7C the fiber was stretched and allowed to dry under tension. All of the x-ray lines exist as equatorial arcs indicating a uniaxial orientation.

The two latter types of orientation described above may be identified in samples of commercial rayons,—the second (figure 7B) in older types, and the third (figure 7C) in modern viscose fibers. The x-ray diagram of a viscose rayon (older type, 1928) is shown in figure 8A. The 101 line

<sup>4</sup> In rayons also, shrinkage will be considered in terms of a small cube located at any section of the fiber. Thus, in shrinkage along one axis in the radial direction, all the shrinkage axes of the cubes would point inward toward the center of the fiber similar to the spokes of a wheel.

exists as a much shorter arc than either the  $10\bar{1}$  or the  $002$  line. This type of diagram, which is similar to that of figure 7B, can be interpreted on the basis of a selective uniplanar orientation, which would result if the fibers were spun without tension, and if, during the formation of the filament, shrinkage were confined largely to the radial direction (figure 6AE). For a selective uniplanar orientation, the  $101$  planes would be parallel to the filament surface and hence in a diffracting position only in the side section of the fiber. As a result the  $101$  lines would exist as equatorial reflections. The  $10\bar{1}$  planes, on the other hand, would be in a diffracting position only at the front and back of the fiber, and since the  $b$ -axes are arranged at random in the surface, the  $10\bar{1}$  line has a random orientation.

If this interpretation is correct, the orientation in the surface of an unstretched rayon filament is similar to that in the surface of a Cellophane sheet and it should be possible to synthesize the same type of x-ray diagram

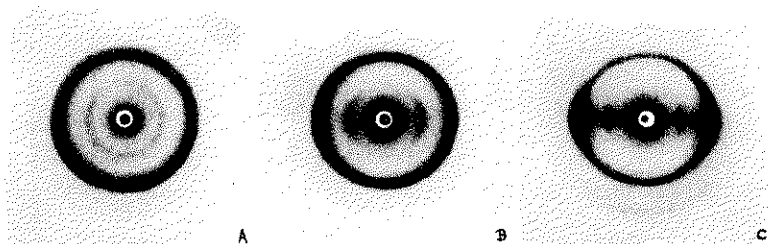


FIG. 7. X-ray diagrams of viscose fibers spun under various conditions: A, allowed to shrink freely; B, not allowed to shrink in length; C, stretched and dried under tension.

by rotating a strip of Cellophane. Figure 8B is the x-ray diagram of a sheet of Cellophane having a selective uniplanar orientation, as shown diagrammatically in figure 8F, with the x-ray beam parallel to the plane of the sheet. The  $101$  planes, being parallel to the surface, diffract strongly as intensity maxima on the equator, the  $10\bar{1}$  faintly on the meridian. Figure 8C is the x-ray diagram with the beam perpendicular to the plane of the Cellophane sheet. The  $101$  plane is not in a diffracting position, but the  $10\bar{1}$  plane is in a diffracting position giving a random orientation (figure 8G). If, therefore, this sheet of Cellophane is rotated during exposure, statistically it should pass through all the angles to the x-ray beam at which sections of the rayon wall are oriented. Figure 8D is the x-ray diagram of the sheet rotated through  $360^\circ$  on a goniometer during exposure. The rotation diagram is almost identical with that of the viscose fiber (figure 8A). Radial shrinkage of the rayon is also indicated by the photomicrograph of the rayon filament (figure 8H), which shows a serrated cross

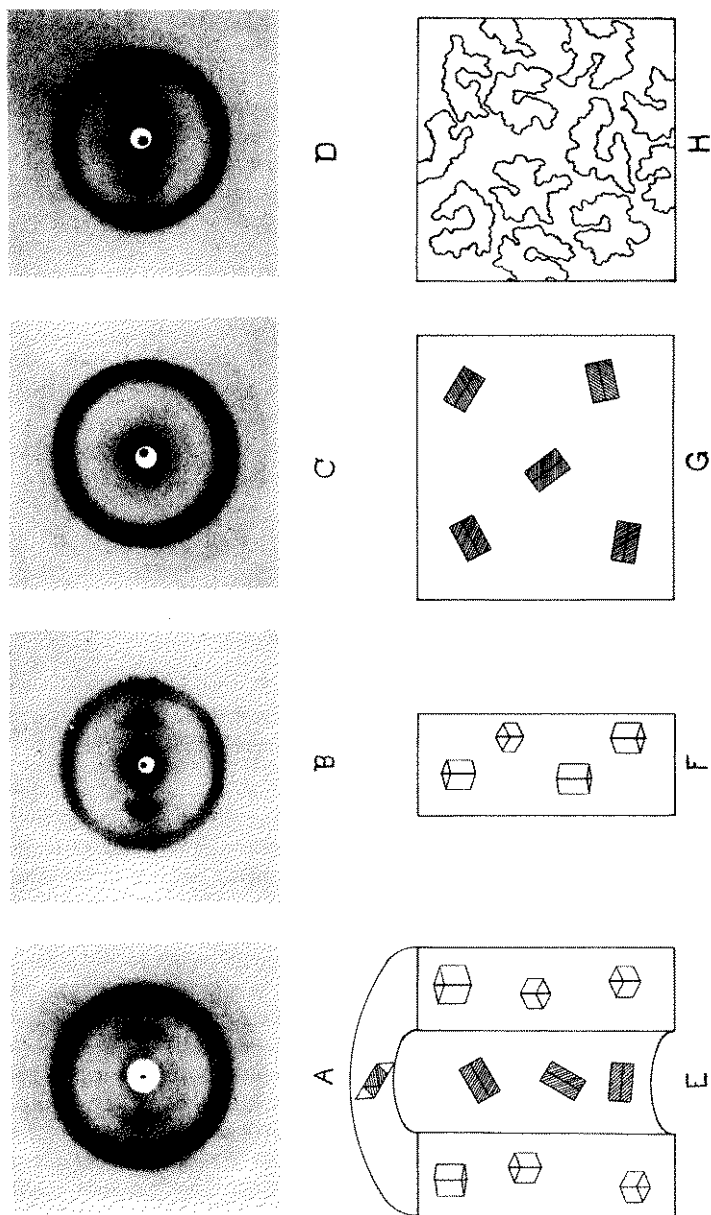


FIG. 8. X-ray diagrams, photomicrographs of cross sections, and schematic representation of orientation in rayons and Cellophane (see text for explanation).

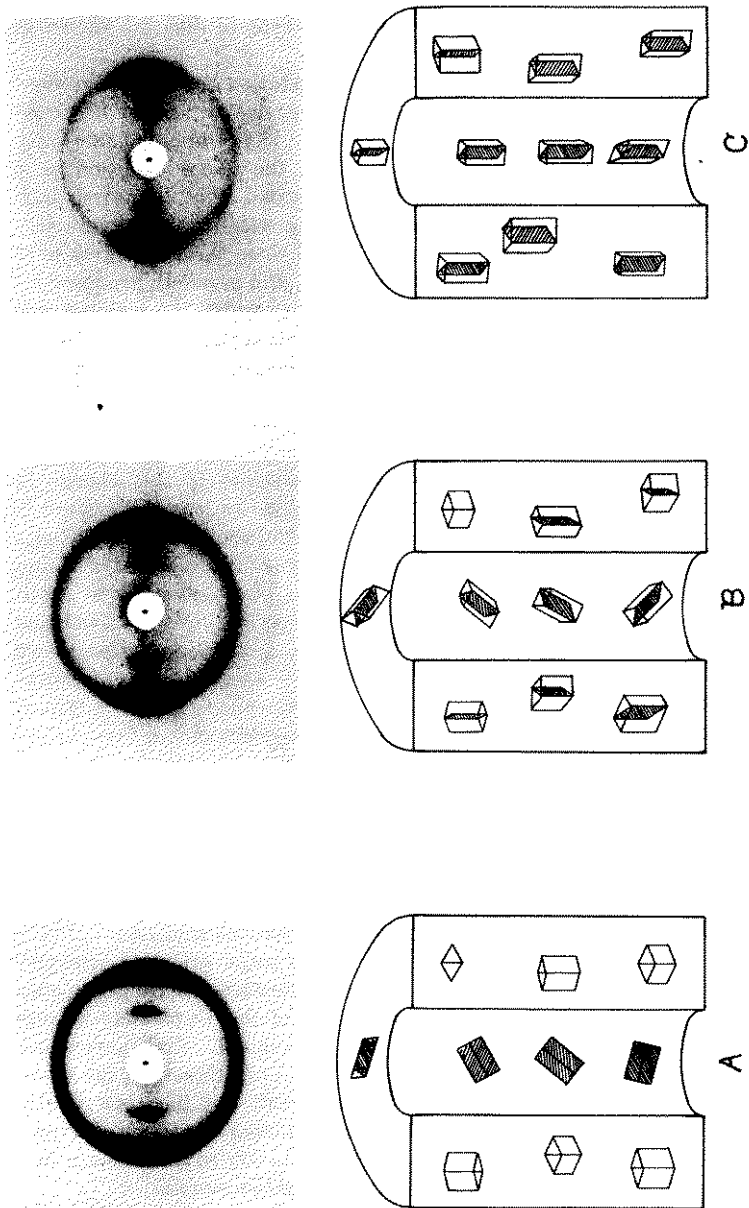


FIG. 9. X-ray diagrams and schematic representation of orientation in three rayon fibers possessing different types of orientation (see text for further explanation).

section. A roll of Cellophane also gives the type of diagram shown in figure 8D.

To the writer's knowledge, this type of orientation has not, heretofore, been recognized in rayons. On the basis of optical studies it has been interpreted erroneously as being due to a more highly oriented skin, produced by hydrodynamical friction set up by the viscose solution as it flows through the jet orifice (1). With polarized light, however, it is difficult to distinguish between a uniaxial and a selective uniplanar orientation in the surface of a rayon filament, and since earlier workers were aware of only two types of orientation (random and parallel), produced by either hydrodynamical friction or the "draft" to which the filament was subjected, it is logical that the optically different surface should be interpreted as being due to a more parallel orientation in the skin, rather than to a selective orientation.

When rayon filaments showing selective orientation are moistened and slowly stretched, the selective orientation is gradually changed to a uniaxial orientation. A diagrammatical representation of this change in orientation and the corresponding x-ray diagrams are shown in figure 9. Figure 9A represents the x-ray diagram and orientation, respectively, of a rayon fiber showing selective orientation. Figure 9B represents an imperfect uniaxial orientation after the fiber has been subjected to about 35 per cent elongation; while figure 9C represents a more perfect uniaxial orientation obtained after stretching 60 per cent. The orientation shown in figure 9A is representative of the average viscose rayon of ten years ago and figure 9B of the average present-day rayon, while figure 9C is typical of the highly stretched special rayons. Most cuprammonium rayons have an orientation approaching that of figure 9C.

#### SUMMARY

Earlier investigations regarding the orienting properties of native cellulose in both natural fibers and in synthetic fibers made from bacterial cellulose membranes have been extended to hydrate cellulose in synthetic fibers produced from cellulose coagulated from various solutions.

The hydrate cellulose crystallite possesses a major orienting tendency with reference to the *b*-axis, and a minor or selective orienting tendency with reference to the 101 plane. Orientation of these axes may be produced either by shrinkage or by elongation of the sample. Whenever there is a relative increase in dimension of a sample in one direction, the *b*-axes of the unit cell tend to orient parallel to that direction; if there is a relative decrease in dimension in one direction, the 101 planes are oriented perpendicular to that direction. The degree of orientation in each case is proportional to the relative change in dimensions of the sample.

In films such as Cellophane, the x-ray diagram shows a selective uni-



planar orientation of the 101 plane if, upon drying, the swollen film is allowed to shrink only normal to the plane of the film. Likewise rayon fibers, especially viscose, if spun without tension, show a similar selective orientation with reference to the fiber surface.

In both films and fibers, selective orientation of the 101 plane is destroyed by stretching, which produces a uniaxial orientation of the *b*-axis (axis of cellulose chains) parallel to the direction of stretching.

#### REFERENCES

- (1) PRESTON, J. M.: J. Soc. Chem. Ind. **50**, 199T (1931).
- (2) SISSON, W. A.: Ind. Eng. Chem. **27**, 51 (1935).
- (3) SISSON, W. A.: J. Phys. Chem. **40**, 343 (1936).
- (4) SISSON, W. A., AND CLARK, G. L.: Ind. Eng. Chem., Anal. Ed. **5**, 296 (1933).
- (5) SNELL, F. D.: Ind. Eng. Chem. **17**, 198 (1925).

#### NEW BOOKS

*Explosions- und Verbrennungsvorgänge in Gasen.* By WILHELM JOST. 16.5 x 24.5 cm.; viii and 608 pp. Berlin: Julius Springer, 1939. Price: 49.50 RM.

Prof. Jost addresses this fine book primarily to German readers, but it will be a most useful addition to the book of Lewis and von Elbe, the U. S. A. Commercial Gas Association's handbook *Combustion*, Laffitte's recent memoir, and Methuen's modest *Chemical Monograph*. (The second and third of these are not mentioned in an almost perfect bibliography.) In so brief a notice, it is easier to enumerate gaps than to particularize in congratulations. Moreover the references almost make good the textual omissions, and there is a subject index of some eighteen hundred entries.

The book is illustrated with hundreds of diagrams, and the odphotographs are excellent; but there are no shadow photographs, and the pictorial photographs are meagre and badly chosen,—a fault that might easily be remedied in a further edition, which also might well expand the too brief chapter 6 into an account of the flames of gas-heated furnaces, and mention Argand, father of all "diffusion-flames," from whose burner, as modified by Frankland, Bunsen's was by one step derived. The modernist trend of the book could indeed be indicated no better than by the omission of Argand, Frankland, Clerk, and Beyling from the long list of seven hundred authors, or by the one mention of Bunsen as compared with the numerous references to Bodenstein or to Semenoff. Another edition might also, despite the superficial limits imposed by the title, say something of the propagation of flames through dusts and sprays. After all, what could be a better introduction to "burning back" than the travelling zone of combustion in a test tube filled with ammonium dichromate or with a mixture of iron filings and sulfur dust, or, for that matter, in a squib?

A chapter on aerodynamics, expanding chapter 4, would be useful, too, in generalizing on the growth of a flame, or of flames, in an explosive medium. One of the innumerable spiral motions in nature, the "spin" of detonation, to which the author gives many pages, would then fall into place as an example among many of how flame travels, with least energy expense, as one fluid through another. "Turbu-