# HORIO LABORATORY (April 1938∼)

## Head: Dr. Masao Horio

The field of research in this laboratory at its outset was originally confined for historical reason to the developing works on pulp and viscose, and the researches were done successfully leading the way in the world in laying foundation of several new processes such as high tenacity rayon spinning (1939), crimped rayon staple process (1939), prehydrolyzed sulphate cooking (1944) and so forth, as illustrated in the previous commemoration issue. The studies have been prosecuted in any time in direct connection with our laboratory of the Department of Polymer Chemistry of Kyoto University in which the fundamental works on the structure of natural and synthetic high polymers are treated. Our colleagues represented by Professor K. Kobayashi and Professor H. Inagaki in this Institute have made eminent achievements in the field of structure study and made a valuable contribution to the Institute by taking office as the heads of the independent Laboratories. The results of their works are to be seen in their own Laboratories' reports. The following are the results of the studies in this Laboratory obtained within these fifteen years.

### I. Pulp, Paper and Wood Chemistry

The prehydrolyzed sulphate cooking developed by us in the war time was planned to be industrialized by Nippon Pulp Industry Co., Ltd. in 1949, and the construction of their new pulp mill at Yonago, Tottori Pref. was commenced in May, 1951. The mill was laid out after the design based upon our developing work performed in this Institute and completed in October, 1952. This is esteemed as one of the first successes in the world in manufacturing the dissolving pulp by the prehydrolyzed sulphate process. The mill produces now about sixty thousand tons of dissolving pulp per year by this new process. A series of our study on the bleached sulphate pulp of hard wood also stimulated the paper industry of this country, which had for a long time sticked to the sulphite process and lead them to convert to the sulphate process. Thus the annual production of sulphate pulp for paper increased its quantity by forty-two times during these fifteen years.

The prehydrolyzed sulphate process was found to be applied successfully to the bamboo also.[1,2,3] The plant was designed after our fundamental works by Japan Consulting Institute which licenced Dawood Industries Ltd., East Pakistan, to construct a mill at Karnaphuli, East Pakistan, which will be ready for production of 35 tons per day of dissolving pulp from bamboo from the end of 1966.

The utilization of agricultural wastes such as bagasse and straw has also been the subject of our study. Recently we succeeded in manufacturing the news paper from bagasse by employing the efficient mechanical refiners.[4,5] The experiments were carried out with success on commercial scale at the Ishinomaki mill, Iwate Pref. of Tohoku Pulp Co., Ltd. in June, 1966.

The tensile strength of paper was studied as a function of fiber strength, texture and uniformity. A new method of dynamic measurements of mechanical properties of pulp and paper was developed, and the dynamic moduli were measured as a function of density, freeness, species of fibers, content of parenchyma and so forth. The angular dependency of molulus, tensile strength and elongation of paper having a definite grain direction was calculated and the theory was tested experimentally.[6]

A series of fundamental studies on hemicellulose have been done together with those of pulp and paper. A study on the light scattering of xylan derivative prepared from beech hemicellulose revealed that the molecules are rather rod-like than coiling.[7]

It could be shown that the hard wood xylan undergoing minimum degradation shows a distinct x-ray diffraction pattern. The mannan-rich fraction of soft wood hemicellulose showed a diffraction pattern similar to that of ivory nut mannan, although considerably diffused. These observations made it possible to characterize the compositions of alkali solubles of various kinds of pulp by x-ray diffraction analysis. The diffraction patterns of gamma cellulose which had not been interpreted before were found to be composed of the peaks characteristic to those of xylan and mannan.[8]

The diffraction patterns having an indication of fiber diagram were obtained with the membranes of xylan stretched by rolling. The diagram could be nearly interpreted on the basis of an end-surface centered rhombic cell whose two axes of the basal plane have exactly the ratio of $\sqrt{3}:1$. The observed reflections could be indexed on the base of orthohexagonal unit cell. The sharpness of the pattern depended upon the content of 4-0-methyl glucuronic acid residue. The xylan specimens which were richer in uronic acid residue than the molar ratio of 1:13 showed only a single diffuse halo.[9]

Taking interest in utilization of vanillic acid which is obtainable from lignin several polyesters were synthesized and spun into filaments. 1,2 bis (2-methoxy-4-carboxy-phenoxy) ethane was derived from vanillic acid, condensed with ethylene glycol and converted into a polyetherester. The polymer is crystalline and spinnable into filaments, but the mechanical properties, resistance to heat and degree of crystallinity are inferior to those of polyetheresters derived from 1,2 bis (2-methyl-4-carboxy-phenoxy) ethane and 1,2 bis (4-carboxy-phenoxy) ethane.[10,11,12]

## II. Rayon and Cellulose Chemistry

The structure of crimped rayon staple was studied[13] together with the development of its manufacturing process, and a new concept of bilateral structure was first introduced in order to interpret the mechanim of crimping of textile fibers. When any one side of each individual viscose filament is more elastic, whilst the other side relatively more plastic, the filament results in making a very fine coil when it is released from stretching. In an assembly made up of a huge number of bilateral filaments packing together closely the individual fibers are prevented from coiling independently and are lead to form altogether a planar wave, as can be seen in the fleece of wool. The mechanim of production of bilateral structure has laid the foundation of the fundamental theory of crimping of textile fibers in general, and opened up a way to fabricate the conjugate fibers.[14,15]

A series of developing works on the continuous process of alkali cellulose preparation making use of a screw press[16] have promoted its industrialization.

The specimens of cellulose xanthate differing in degree of xanthation were converted into methyl cellulose by replacing the dithiocarbonic acid residues with methyl residues, and the hydrolyzates were separated into components by the chromatographic technique. It was ascertained that the 2-positioned OH is most accessible to xanthation reaction, while the 3-positioned one is most resistant to the xanthation reagent. The quantities of glucose, 2-*o*-methyl, 3-*o*-methyl, 6-*o*-methyl, 2,3-di-*o*-methyl, 2,6-di-*o*-methyl and 3,6-di-*o*-methyl glucose in the hydrolyzates of methylated products were measured, and the distribution of xanthate residues in cellulose xanthate was discussed as a function of degree of xanthation.[17,18]

The spinning of cellulose acetate by the dry process was studied in detail from the technical point of view.[19]

The non-Newtonian character of cellulose solutions was studied as a function of the concentration of cellulose and the rate of shear.[20]

A series of studies on photodegradation of cellulose have been done and the mechanism was discussed.[21]

The selective uniplanar orientation of (101) plane of cellulose crystal at the coagulation of viscose was discussed.[22] It could be shown that the planar orientation takes place more prominently with increasing contents of sulphates in the precipitation bath. The orientation is conditioned by the dehydration of viscose during coagulation; Because of the hydrophilic character of (101) plane, it is forced to face to the direction of water flow, or, in other words, it is arranged parallel to the surface of fiber or film made from that viscose. The fibers or films having the uniplanar orientation show very different swelling properties from those of isotropic materials, because water penetrates mostly into the spaces between (101) planes. The production of Cellulose IV at the viscose spinning was discussed.

## III. Radiation Chemical Studies

A series of gamma-ray irradiation researches on polymers have been done by the courtesy of Professor S. Shimizu of this Institute who installed the $Co^{60}$ gamma-ray facility for the advancement of radiation studies in this Institute. The cotton linter and wood pulp were irradiated with various radiation doses and the $DP_n$'s were measured.[23] The following relation was obtained among the initial $DP$ ($P_0$), the DP after irradiation ($P$) and the radiation dose ($R$) in million *r*.

$$1/P - 1/P_0 = 0.76 \cdot R^{0.85}$$

The electron microscopic observations showed that the crystallites are shortened by irradiation. The paper chromatographic measurements of hydrolyzates of irradiated cotton showed that the glucose residues in cellulose are partially converted into the glucuronic acid, xylose and arabinose residues. The mass-spectrometer analysis of gas evolved during irradiation showed that it is chiefly hydrogen.

The effect of gamma irradiation upon wool fibers was studied.[24] The statistical analysis of tensile strength and elastic modulus as a function of dose resulted in the conclusion that no appreciable change in mechanical properties is produced by the doses below $10^7 r$. The radiation damage of fibers is prominent at the irradiation above $10^8 r$. The dyeing property is noticeably influenced by irradiation. The solubility tests suggested that the cross-linking would have been produced by irradiation.

The studies on the graft copolymerization of synthetic polymers onto viscose rayon has been done since more than ten years ago, although they are published rather recently.[25,26,27]

The modification of wool by graft copolymerization of styrene, methyl methacrylate and acrylonitrile onto fibers under irradiation was also studied.[28]

The preparation of low viscosity pulp by gamma-ray irradiation was also studied from the technical point of view.[29] The use of this pulp eliminates the step of aging of alkali cellulose and facilitates the emulsion xanthation.

## IV. Bilateral Structure of Wool

The theory of bilateral structure of textile fibers could be applied successfully to wool fibers also.[30,31] Individual wool fibers having fine crimps consist of two cortical segments which exist bilaterally throughout entire length of fibers and differ in dyeing property and resistance to various reagents. This theory has been accepted widely in the world, and it was suggested at the 1st International Wool Textile Research Conference held in Melbourne in 1955, to call tentatively the segment locating on the outside of curvature of crimp the "ortho-cortex", and the one locating on the inside of curvature the "para-cortex". A series of papers relative to the sturcture and modification of wool fibers have been published in this Bulletin.[32,33,34] The pyrolysis[35] and the chemical modificatoin[36] of wool also revealed the new evidences of bilateral structure.

## V. Mechanical Properties and Structure of High Polymers

The theoretical background of vibration reed method[37] and dynamic mesaurements of mechanical properties of various high polymers[38] were developed. Measurements of birefringence were introduced into the rheological studies.[39,40,41,42,43,44] Effects of temperature and blending on the rheological properties of polyethylene melts[45] were studied by constructing a universal rheometer.[46] The orientation of crystallographic axes and planes in polymer sheets was discussed.[47]

## Publications

(* indicates an article published in Japanese)

1. M. Horio and M. Takahama: Manufacture of Dissolving Pulp from Bamboo, Pakistan Pat. 108353, 108354, 108355 (1957).
2. M. Horio and M. Takahama: Dissovling Pulp from Bamboo, Japan Consulting Institute, August, November and December, 1957.

3. M. Horio and M. Takahama: Manufacture of Dissolving Pulp from Indian and Pakistan Bamboo, *Proc. Res. Inst. Synthetic Fibers, Japan,* **16,** 187 (1959).*
4. M. Horio, R. Imamura and S. Yamashita: Fundamental Studies on the Manufacture of the News Paper from Bagasse by Mechanical Process, Japan Consulting Institute, March, 1965.*
5. M. Horio, R. Imamura and S. Yamashita: Fundamental Studies on the Manufacture of the News Paper from Bagasse by Mechanical Process (Continued report), Japan Consulting Institute, November, 1966.*
6. M. Horio and S. Onogi: Dynamic Measurements of Physical Properties of Pulp and Paper by Audiofrequency Sound, *J. Appl. Phys.,* **22,** 971 (1951); S. Onogi, S. Ando and T. Yamamoto, *J. Chem. Ind., Japan,* **57,** 251 (1954).
7. M. Horio, R. Imamura and H. Inagaki: A Study of Light Scattering on Xylan, Tappi, **38,** 216 (1955).
8. M. Horio, R. Imamura and K. Tani: Characterization of Alkali Solubles by X-Ray Diffraction Analysis, Tappi, **43,** 769 (1960).
9. M. Horio and R. Imamura: Crystallographic Study of Xylan from Wood, *J. Polymer Sci., A,* **2,** 627 (1964).
10. M. Horio, R. Imamura, T. Kiyotsukuri and K. Kuroda: Studies on the Synthetic Fiber derived from Vanillic Acid, *Proc. Res. Inst. Synthetic Fibers, Japan,* **17,** 51 (1960).*
11. M. Horio, R. Imamura, T. Kiyotsukuri and K. Kuroda: Effects of Side Substituents of the Benzene Nuclei for Aromatic Polyesterether Homologs, *Proc. Res. Inst. Synthetic Fibers, Japan,* **19,** 43 (1962).*
12. R. Imamura, Y. Yamamoto and T. Kiyotsukuri and O. Sangen: Crystallographic Behavior of Aromatic Polyesters with Side Groups, International Symposium of Macromolecular Chemistry, Tokyo and Kyoto, 3–5–11, 1966.
13. M. Horio and T. Kondo: Theory and Morphology of Crimped Rayon Staple, *Textile Research J.,* **23,** 137 (1953).
14. M. Horio: The Theory of Crimp of Textile Fibers, *Mem. Faculty of Engineering, Kyoto Univ.,* **26,** 222 (1964).
15. M. Horio: Conjugate Fibers, *Proc. Res. Inst. Synthetic Fibers, Japan,* **21,** 79 (1964).* See E.M. Hicks, J.F. Ryan, R.B. Taylor and R.L. Tichenor, *Textile Research J.,* **30,** 675 (1960).
16. M. Horio and M. Takahama: Continuous Process for the Manufacture of Viscose, *Proc. Res. Inst. Synthetic Fibers, Japan,* **11,** 164 (1954).*
17. M. Horio, R. Imamura and A. Sakata: Studies on the Distribution of Xanthate groups, *J. Soc. Textile and Cellulose Ind., Japan,* **14,** 909 (1958).*
18. M. Horio, R. Imamura, N. Komatsu, A. Sakata and N. Kato: The Study on the Mechanism of the Cellulose Reaction. (II) The Investigation on the Distribution of Xanthate Groups in the Various Cellulose Xanthates by Means of the Paper Chromatography. (III) The Discussion on the Locating Selectivity of Xanthate Groups, *J. Soc. Textile and Cellulose Ind., Japan,* **19,** 102 (1963).*
19. M. Horio and M. Takahama: Spinning of Cellulose Acetate, *Proc. Res. Inst. Synthetic Fibers, Japan,* **12,** 87 (1955).*
20. M. Horio, S. Onogi, Y. Taniguchi, T. Kobayashi and K. Kuroda: The Effect of Velocity Gradient and Cellulose Concentration on Viscosities of Cellulose Solutions, *J. Soc. Textile and Cellulose Ind., Japan,* **13,** 830 (1957).*
21. C. Kujirai: Studies on the Photodegradation of Cellulose. (I) Absorption Spectrum of Cellulose and Experimental Method of Photodegradation. (II) Fundamental Experiments on the Photodegradation Cellulose. (III) Ultra-violet Absorption Spectra of Cellulose Peroxide, *J. Soc. Textile and Cellulose Ind., Japan,* **21,** 183, 190, 260, 626, 631 (1965).*
22. M. Horio, K. Kobayashi and T. Takahashi: Orientation of (101) Planes of Cellulose during Fiber and Sheet Formation from Viscose, International Symposium of Macromolecular Chemistry, Tokyo and Kyoto, 4–5–15 (1966).
23. M. Horio, R. Imamura and H. Mizugami: Effect of Gamma Irradiation upon Cellulose, THIS BULLETIN, **41,** 17 (1963).

24. M. Horio, K. Ogami, T. Kondo and K. Sekimoto: Effect of Gamma Irradiation upon Wool Fibers, THIS BULLETIN, **41,** 1 (1963).
25. R. Imamura, T. Taga and H. Inagaki: Studies of Graft Copolymerization onto Viscose Rayon, *J. Soc. Textile and Cellulose Ind., Japan,* **21,** 303 (1965).*
26. R. Imamura, T. Taga, S. Washijima and M. Otaguro: Graft Copolymerization of Acrylonitrile by Simultaneous Irradiation Method of $Co^{60}$ $\gamma$-ray, *J. Soc. Textile and Cellulose Ind., Japan,* **21,** 349 (1965).*
27. T. Taga, R. Imamura and M. Horio: To be presented before the XXth Annual Meeting of Chemical Socity of Japan, April, 1967.
28. M. Horio, K. Ogami, T. Kondo and K. Sekimoto: Polymerization of Styrene, Methyl Methacrylate and Acrylonitrile onto Wool by Gamma Irradiation, THIS BULLETIN, **40,** 10 (1963).
29. R. Imamura, S. Yamashita and H. Mizugami: Studies of the Low Viscosity Pulp by Gamma-Ray Irradiation, *Proc. Res. Inst. Synthetic Fibers, Japan,* **16,** 131 (1959).*
30. M. Horio and T. Kondo: Crimping of Wool Fibers, *Textile Research J.,* **23,** 373 (1953).
31. M. Horio, T. Kondo, K. Sekimoto and A. Teramoto: Bilateralstrukture der Wolle, *Z. Naturforschung,* **15,** 343 (1960).
32. M. Horio, C. Sakai, T. Kondo and K. Sekimoto: Shrinkproofing of Wool by Permanganate/Sodium Chloride Treatment, THIS BULLETIN, **40,** 351 (1962).
33. M. Horio, C. Sakai, T. Kondo and K. Sekimoto: Comparison between the Effect of Permanganate/Sodium Chloride and That of Permanganate/Water upon Wool, THIS BULLETIN, **40,** 358 (1962).
34. M. Horio, M. Funatsu, T. Kondo and K. Sekimoto: Application of Interfacial Polymerization upon Wool, THIS BULLETIN, **42,** 153 (1964).
35. M. Horio, T. Kondo, K. Sekimoto and M. Funatsu: Pyrolysis of Wool in Sealed Tubes, *Proc.* IIIth International Wool Textile Research Conference, Vol. 2, 189 (1965).
36. M. Horio, T. Kondo, Y. Nakamura, H. Sugiyama, K. Nishiumi and M. Tani: Histochemical Studies on Chemically Modified Wool, International Symposium on Macromolecular Chemistry, Tokyo and Kyoto, 15–0–4, (1966).
37. M. Horio and S. Onogi: Forced Vibration of Reed as a Method of Determining Viscoelasticity, *J. Appl. Phys.,* **22,** 977 (1951).
38. M. Horio, S. Onogi, C. Nakayama and K. Yamamoto: Dynamic Measurements of Physical Properties of Pulp and Paper by Audiofrequency Sound, *J. Appl. Phys.,* **22,** 971 (1951).
39. M. Horio: Rheological and Optical Properties of Cellulose, International Congress of Pure and Applied Chemistry, New York, (1951).
40. M. Horio and T. Kondo: Reo-optical Properties of Fibers, *J. Soc. Material Testing,* **11,** 256 (1957).*
41. T. Kondo, I. Terasaki and R. Yamada: Reo-optical Properties of Polymers, *Proc. Res. Inst. Synthetic Fibers, Japan,* **13,** 29 (1956).*
42. N. Utsumi: Stretch Birefringence of Polymer Films, *Proc. Res. Inst. Synthetic Fibers, Japan,* **15,** 31 (1958).*
43. R. Yamada, C. Hayashi, S. Onogi and M. Horio: Dynamic Birefringence of Several High Polymers, *J. Polymer Sci., C,* 123 (1963).
44. N. Utsumi: The Photoviscoelastic Investigation of High Polymeric Films, (I) The Stress Relaxation in Natural Rubber and its Birefringence and Crystallization. (II) The Stress Relaxation and Birefringence of Polyvinylchloride Films and the Temperature Dependency of their Strain Birefringence, *J. Soc. Textile and Cellulose Ind., Japan,* **21,** 239, 293 (1965).*
45. M. Horio, T. Fujii and S. Onogi: Rheological Properties of Polyethylene Melts: Effects of Temperature and Blending, *J. Phys. Chem.,* **68,** 778 (1964).
46. M. Horio, S. Onogi and S. Ogiwara: A Rheometer for Measuring the Viscoelasticity of High Polymer Melts, *J. Soc. Material Testing,* **10,** 350 (1961).*
47. M. Horio: The Deformation Process and Structure of Crystalline Polymers, General Lecture at the IVth International Congress on Rheology, (1963). *Proceedings of the Congress, Vol. 1, 29 (1965).*