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Studies of Ion Exchange Membranes. XXXI. The Hydrogen Peroxide Treatment of the Cation Exchange Membrane of Ferric Ion Form

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Neosepta CL-2.5T, the cation-exchange membrane prepared by the "Paste Method," of the ferric-ion form was treated with hydrogen peroxide, and the changes in the membrane properties (the thickness, the water content, and the ion-exchange capacity) were measured. The porous membrane, having no ion-exchange capacity, was obtained by the treatment with hydrogen peroxide and the water permeation through the membrane was measured. Assuming the capillary model, the water-permeability data of this membrane suggested that the apparent pore radius of this membrane was 15—17 mμ and that the apparent pore distance was about 40 mμ. This suggests that Neosepta CL-2.5T contains a minute and continuous heterogeneity; *i.e.*, there is a localized distribution of the ion-exchange resin component within the membrane.

The present author has previously proposed the "Paste Method"[1-4] as a practical procedure for the preparation of an ion-exchange membrane. In this procedure, a fine powder of polyvinyl chloride (PVC) and a monomer mixture, mainly consisting of styrene (St) and divinylbenzene (DVB), were mixed to prepare a paste, and then this paste was coated onto Teviron cloth (a reinforcing material). The resultant polymer composite was heated to polymerize the monomers and to convert the PVC powder to a PVC gel. Then, an ion-exchange group was introduced to the base membrane by sulfonation or chloromethylation and amination with trimethylamine. The ion-exchange membrane thus prepared (commercial name, Neosepta) has been used in electrodialytic concentration[5-7] or in the desalination of sea water.[8] One of the characteristic properties of this ion-exchange membrane is its excellent flexibility, which makes it easy to handle the membrane in practical use; this fact also suggests that the structure of the membrane may be different from a rigid gel-structure such as, for example, that of amberlite IR-120.

In a preceding paper,[9] the chemical structure of the ion-exchange membrane prepared by the "Paste Method" was studied by means of extraction with tetrahydrofuran and it was concluded that the fine powdery ion-exchange resin component, extractable through a filter paper with tetrahydrofuran, was present, while the matrix of the ion-exchange resin component was complicatedly entwined with the PVC chain and there was a graft copolymer of the former onto the latter. In this study, the chemical structure of the ion-exchange membrane prepared by the "Paste Method" was investigated by making use of the treatment with hydrogen peroxide.

Experimental

The Sample. Prior to the experiment, Neosepta CL-2.5T was treated alternately with 0.1N aqueous solutions of sodium chloride and hydrochloric acid; thus the membrane properties were made stationary. The ion-exchange capacity, the thickness, and the water content were measured at 21°C by ordinary methods.

The Treatment with Hydrogen Peroxide. After Neosepta CL-2.5T of the hydrogen-ion form had been soaked in an aqueous solution of ferric chloride (0.15 mol/*l*), the surface of the membrane was wiped with a filter paper and the membrane was soaked in an aqueous solution of hydrogen peroxide (5—6%) at room temperature with intermittent stirring.

The Measurement of the Water Permeability. The apparatus is shown in Fig. 1. The pressure difference (Δp) between the both sides of the membrane

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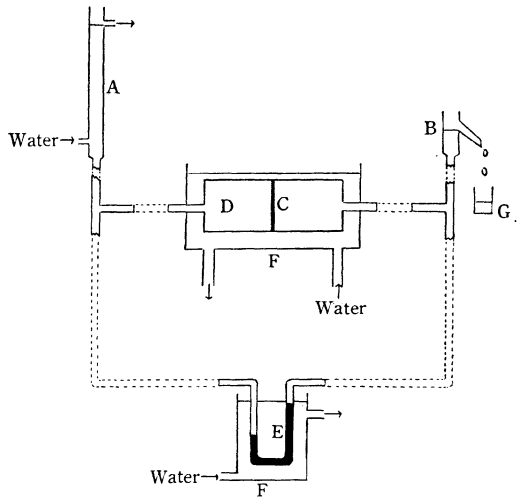

Fig. 1. The apparatus.
A, B: Leveling bulb C: Membrane
D: Cell E: Hg differential manometer
F: Thermostat G: Weighing bottle

was measured by means of the mercury differential manometer (E). While the Δp value was kept constant, the water permeating in a given period was collected in a weighing bottle (G) and weighed. The temperature of the thermostat (F) was 21°C. The effective area of the membrane was 20 cm².

Characterization of the Water Permeability Through the Membrane. The size and the number of pores of a porous diaphragm can be calculated by applying D'Arcy's law and Poiseuille's law, as has been done for a porcelain diaphragm by Sanada.[10] The following equation is well-known as D'Arcy's law, relating to water permeability through a porous membrane:

$$K_p = \frac{Q\eta L}{A\Delta p} \tag{1}$$

where K_p is the specific permeability (cm²); Q, the permeation rate (cm³/sec); A, the effective area of the membrane (cm²); η, the viscosity of water (poise); Δp, the pressure difference (dyne/cm²), and L, the thickness of the membrane (cm).

Assuming that a pore is cylindrical and that it is vertical to the membrane plane and does not intercross with it, Poiseuille's law (Eq. (2)) can be applied to the water permeation through the pore:

$$V = \frac{\pi r^4 \Delta p}{8\eta L} \tag{2}$$

where r is the pore radius (cm) and V, the permeation rate through a pore (cm³/sec). Therefore, the permeation rate through the porous membrane can be expressed as follows:

$$Q = \frac{nA\pi r^4 \Delta p}{8\eta L} \tag{3}$$

where n is the pore number/cm².

On the other hand, the porosity of the membrane (ε) is given by Eq. (4):

$$\varepsilon = \frac{W_e - W_d}{AL\rho_w} = \pi r^2 n \tag{4}$$

where W_e is the wet weight of the membrane (g); W_d, the dry weight of the membrane (g), and ρ_w, the specific gravity of water. By comparing Eqs. (1), (3), and (4), Eqs. (5) and (6) can be derived:

$$r = \sqrt{\frac{8\pi LQ}{\varepsilon A\Delta p}} = \sqrt{\frac{8}{\varepsilon}K_p} \tag{5}$$

$$n = \frac{\varepsilon^2}{8\pi K_p} \tag{6}$$

Assuming the square array of the pores, the apparent pore distance (δ, cm) can be given by Eq. (7).

$$\delta = \frac{1}{\sqrt{n}} \tag{7}$$

Results and Discussion

As a preliminary, it was confirmed that Amberlite IR-120 was completely decomposed by the treatment with hydrogen peroxide, while PVC was essentially stable under the same treatment.

Figure 2 shows the change in the membrane

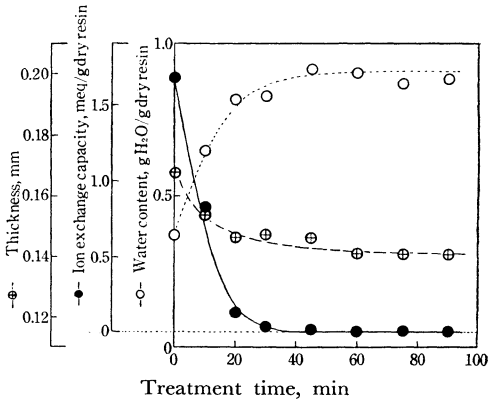

Fig. 2. The membrane properties *vs.* the treatment time with hydrogen peroxide.

properties *vs.* the treatment time with hydrogen peroxide. After 40 min, the thickness and the water content became constant, and the ion-exchange capacity was completely lost. The decrease in the thickness can be attributed to the decrease in the swelling pressure due to lack of the ion-exchange group. Contrary to the decrease in the thickness, the water content increased. This can be explained by the increase in the membrane porosity caused by the decomposition of the ion-exchange resin component within the membrane.

Figure 3 shows the dry weight of the membrane against the treatment time with hydrogen peroxide. After more than 40 min, constant values were observed. Table 1 shows the change in the chlorine content of the membrane *vs.* the treatment time with hydrogen peroxide. The chlorine content gradually decreased with the increase in the treatment time, approaching a constant value after 75—90 min. However, the decreased chlorine contents

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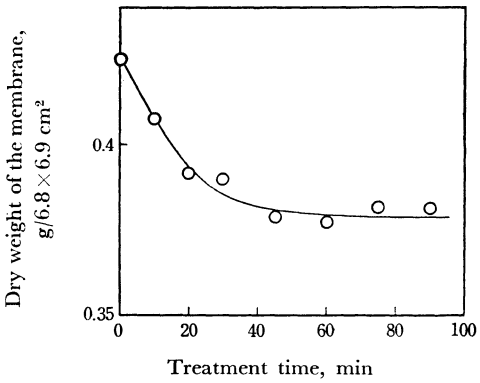

Fig. 3. Dry weight of the membrane *vs.* the treatment time with hydrogen peroxide.

Table 1. The chlorine content of the membrane treated with hydrogen peroxide

Treatment time, min	45	60	75	90
Cl content, %	54.82	54.74	54.08	54.12

are less than that of polyvinyl chloride itself (56.4%). This indicates the treatment with hydrogen peroxide caused not only the decomposition of the ion-exchange resin component but also a slight decomposition of the polyvinyl chloride.

Thus, Neosepta CL-2.5T was transformed to a pale yellowish brown membrane after the complete decomposition of the ion-exchange resin component, and the resultant membrane showed definite properties and an appreciable water permeability, indicating that the membrane was porous. Figure 4

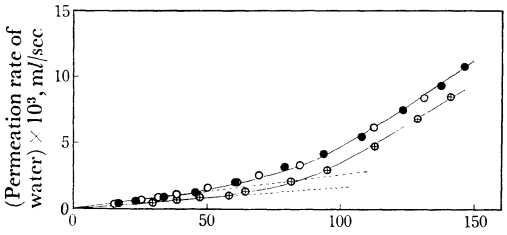

Fig. 4. The permeation rate of water *vs.* the pressure difference between both sides of the membrane.
Treatment time
⊕: 45 min ●: 75 min ○: 90 min

shows the experimental results on the water permeation. When Δp is small, a linear relation was observed between the permeation rate of water and Δp. From the slopes of this straight line, the specific permeation rate was calculated according to Eq. (1). The calculated values are cited in Table 2. As is shown in Table 2, the apparent pore radius is 15—17 mμ, and the apparent pore distance, about 40 mμ.

Table 2. The experimental results

Treatment time, min	45	75	90
$(Q/\Delta p)\times 10^8$, cm⁵/sec·g	1.84	2.65	2.65
$K_p\times 10^{13}$, cm²	1.26	1.81	1.81
ε	0.500	0.509	0.513
$r\times 10^6$, cm	1.5	1.7	1.7
$n\times 10^{-10}$, cm^{-2}	7.9	5.7	5.8
$\delta\times 10^6$, cm	3.6	4.2	4.2

η: 0.981 centipoise at 21°C

These values are in good agreement with the results of the previous paper,[9] in which there was a fine powdery cation-exchange resin component of 50 mμ or less in the cation-exchange membrane prepared by the "Paste Method." Furthermore, the obtained result suggests that the structure of Neosepta CL-2.5T is different from that of both Amberlite IR-120 having a rigid gel-structure and that of a mosaic-type membrane[11,12] having a discontinuous heterogeneity of the ion-exchange resin component.

A membrane structure such as that described above may be comprehended by considering the mechanism of the process of preparing the base membrane. Since St and DVB were polymerized in a gel phase of PVC, the St-DVB matrix should be complicatedly entwined with the PVC chain and the former should be grafted onto the latter. This may be supported by the fact that a graft copolymer is formed when St is polymerized in a PVC film.[13] These facts should be effective in improving the homogeneity of the membrane. However, while a gel phase of PVC is comiscible with both St and DVB, it is immiscible with polystyrene; thus, the resultant polymer should be separated in a fine powdery form. This may be deduced from the fact that a fine powdery polymer is obtained when *n*-heptane, which is comiscible with both monomers but immiscible with polystyrene, is used in place of PVC.[14,15] This should engender the heterogeneity of the membrane and, in fact, is probably the reason why Neosepta CL-2.5T was transformed into the microporous membrane with no ion-exchange capacity upon treatment with hydrogen peroxide.

In conclusion, Neosepta CL-2.5T contains a minute and continuous heterogeneity; *i.e.*, there is a localized distribution of the ion-exchange resin component. Furthermore, the excellent flexibility of Neosepta CL-2.5T may be attributed to the heterogeneity described above. Further details will be investigated in the future.

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