Studies of Ion Exchange Membranes. XXII. Semicontinuous Preparation of Ion Exchange Membranes by the "Paste Method"[1]

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Previous work in this series[2] has presented a method for the preparation of ion exchange membranes called the "paste method," in which paste I, composed of styrene (St), divinylbenzene (DVB), and poly(vinyl chloride) fine powder (PVC), or paste II, composed of St, DVB, 2-methyl-5-vinylpyridine (MVP), and PVC, was coated onto the cloth or the net of the synthetic resin and then heated in order to prepare the polymer film backed with a reinforcing material (Base Membrane), to which the ion exchange group was then introduced by appropriate after-treatments.

The preparative method previously described was excellent in terms of its ease and the mechanical and electrochemical properties of the products, but it was unsuited as a continuous preparative process.

The present investigation was, therefore, undertaken to develop the paste method into a continuous process. In the first stage the continuous preparation of the base membrane was attempted.

The roll coating system being employed, the process of the coating could be carried out continuously, thus obtaining a base membrane 1 m. wide and 50 m. long with a good uniformity. The preparative methods of the base membrane and the ion exchange membrane will be described, and the properties of the products will be discussed in relation to the preparative conditions.

Experimental

The Preparation of the Paste. — Table I shows some typical compositions of the pastes. The components of the paste were mixed to disperse PVC homogeneously, and then the paste was kept for 16 hr. at 20°C (paste I) or 10°C (paste II) in order to stabilize its properties. Prior to coating, the paste was filtered through a 50-mesh polyethylene screen.

Coating.—Figure 1 shows the roll coating system. The wind-up roll 3 was the only driven roll; the others were idler rolls. The reinforcing material reserved to roll 1 was tensioned in its length by the application of the brake on roll 1, expanded in its width by the expander roll 5, and then dipped in the paste in the paste reservoir 4. The covering material which was fed from roll 2 was tensioned and expaned in the same ways as the reinforcing material. The reinforcing material coated with the paste was wound up on roll 3 with the covering material in layers. The pressure which was placed on roll 3 by roll 6 adjusted the quantity of the paste coated onto the reinforcing material. The reinforcing material, 1 m. wide and 50 m. long, was coated once.

Heating. — After the coating process, roll 3 was dismantled, cramped with iron shackles at the hems of the wound reinforcing material, thus preventing the reinforcing material from shrinking

TABLE I. TYPICAL COMPOSITIONS OF THE PASTES

Component	Paste I	Paste II
PVC*1	1.00	1
St	2.3	0.22
DVB*2	0.3	0.14
MVP	—	1.44
Dioctyl phthalate (DOP)	0.3	0.30
Benzoyl peroxide (BPO)	0.025	0.03

*1 Sumilit PX-A from the Sumitomo Kagaku Co., Ltd.
*2 Purity of 50% by weight.

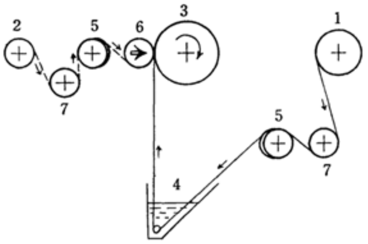

Fig. 1. Coating system.

1 A reserve roll of the reinforcing material, 150 $\phi\times$1250
2 A reserve roll of the covering material, 50 $\phi\times$1250
3 A wind-up roll, 215 $\phi\times$1250
4 A paste reservoir, 28 l.
5 Expander rolls, 115 $\phi\times$1250
6 A press roll, 95 $\phi\times$1250
7 Guide rolls, 95 $\phi\times$1250

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[1] Presented at the 12th Annual Meeting of the Society of Polymer Science Japan, Tokyo, May, 1963.
[2] Y. Mizutani, R. Yamane, H. Ihara and H. Motomura, This Bulletin, 36, 361 (1963).

in width during heating, and then heated at 80—120°C for an hour under high nitrogen pressure (5 kg./cm^2) and then at 80°C for 4 hr. The poly(vinyl chloride) was fused to the continuous film, the monomers were polymerized for the first heating, and the polymerization was completed for the second heating. By being unwound from the roll and torn off from the covering material, the base membrane was obtained.

The Introduction of the Ion Exchange Group to the Base Membrane.—The ion exchange group was introduced to the base membrane by the after treatments described earlier.2) Typical conditions of the after-treatments are shown in Table II.

TABLE II. TYPICAL CONDITIONS OF THE AFTER-TREATMENTS

Active group	Paste	After-treatment
Cation exchange	I	Sulfonation with sulfuric acid (98%) at 60°C for 12 hr.
Anion exchange	II	Quanternization with petroleum ether solution of methyl iodide (methyl iodide/petroleum ether=1/4 by vol.) at 25°C for 24 hr.

Measurements. — *Mechanical Strength.* — Mullen test—burst strength was measured. In the case of the ion exchange membrane, measurement was carried out on a test piece equilibrated with a 0.5 N aqueous solution of sodium chloride.

Expansion by the After-treatment. — Expansion was shown as a ratio of the length of the ion exchange membrane, equilibrated with a 0.5 N aqueous solution of sodium chloride, to that of the base membrane before the after-treatment. Measurement was carried out in the direction of the width of reinforcing material.

Electrochemical Properties. — The water content, ion exchange capacity, electric resistance, and transport number were measured at 25°C according to the procedures described before.2) Electric resistance was measured on a membrane dipped in a 0.5 N aqueous solution of sodium chloride. The transport number was calculated by Nernst's equation from the membrane potential of a concentration cell composed of 0.5 N and 2.5 N aqueous solutions of sodium chloride, separated from each other by the ion exchange membrane under consideration.

Results and Discussion

In relation to the continuous preparation of the base membrane by the roll coating system, the composition of a paste, the choice of a reinforcing material, the choice of a covering material, the conditions of the coating, and the conditions of the heating were investigated.

The Composition of a Paste. — The composition of a paste, which was decided mainly on the basis of the electrochemical properties of the ion exchange membrane,2) also affected its viscosity, which was a main factor in the coating process, and the mechanical properties of the ion exchange membrane.

Table III shows the mechanical and electrochemical properties of the base membrane and the cation exchange membrane in relation to the composition of paste I.

The burst strength of the base membrane did not appreciably change with a weight ratio of either R/PVC or DVB/R, where R was St+DVB or St+DVB+MVP, while that of the ion exchange membrane decreased with an increasing R/PVC. This may be attributed to the brittleness of the sulfonated styrene-divinylbenzene copolymer. The expansion by sulfonation increased with an increasing R/PVC because of the swelling of the styrene-divinylbenzene copolymer through sulfonation.

Reinforcing Material. — To provide the ion exchange membrane with mechanical strength and dimensional stability, the following characteristics are required in the reinforcing material: dimensional stability, adhesiveness with the ion exchange resin, and chemical stability in the processes of the preparation and the application.

TABLE III. COMPOSITIONS OF THE PASTES—PROPERTIES OF THE BASE MEMBRANES AND THE ION EXCHANGE MEMBRANES

Paste		I					
Reinforcing material		Teviron-A					
Composition of the paste by weight	R/PVC	0.8	1.7	2.5	1.7	1.7	1.7
	DVB/R	0.04	0.04	0.04	0.025	0.07	0.10
	DOP/PVC			0.3			
	BPO/R			0.01			
Temperature of the first heating, °C				115			
Burst strength of the base membrane, kg./cm^2		6.3	6.7	6.5	6.8	6.9	6.2
Expansion by the after-treatment*1		1.03	1.05	1.09	1.05	1.05	1.05
Ion exchange membrane	Burst strength, kg./cm^2	5.3	4.6	3.6	4.5	4.5	4.4
	Electric resistance, Ω·cm^2	5.0	2.6	1.8	2.3	4.1	5.3
	Transport number	0.87	0.87	0.85	0.86	0.87	0.87

*1 Condition of the after-treatment: see Table II.

Table IV. Properties of the reinforcing materials

	Dimensional stability	Chemical stability	Adhesiveness with the ion exchange resin	Electrochemical properties of the ion exchange membrane
Cation exchange membrane				
Vinylchloride - vinyliden chloride copolymer net	○	○	△	×
Poly(vinyl chloride) net	△	○	○	×
Polyethylene net	○	○	△	×
Poly(vinyl chloride) cloth	△	○	○	○
Polypropylene cloth	○	○	△	△
Polyacrylonitrile cloth	△	×	○	—
Poly(vinyl alcohol) cloth	○	×	×	—
Poly(ethylene terephthalate) cloth	○	×	△	—
Anion exchange membrane				
Vinylchloride - vinyliden chloride copolymer net	○	×	△	×
Poly(vinyl chloride) net	△	○	○	×
Polyethylene net	○	○	△	×
Poly(vinyl chloride) cloth	△	○	○	○
Polypropylene cloth	○	○	△	○
Polyacrylonitrile cloth	×	○	○	△
Poly(vinyl alcohol) cloth	○	○	×	△
Poly(ethylene terephthalate) cloth	○	○	△	○

○ : good, △ : fair, × : poor, — : could not be judged

Table V. The resin ratios—electrochemical properties of the ion exchange membranes

	Paste	Reinforcing material	Resin ratio g./g.	Ion exchange membrane		
				Thickness mm.	Electric resistance $\Omega\cdot cm^2$	Transport number
Cation exchange membrane	I	Teviron-A	1.09	0.180	4.7	0.87
			1.26	0.190	4.6	0.87
			1.44	0.210	4.5	0.88
			1.58	0.230	4.5	0.88
			1.79	0.235	4.7	0.87
Anion exchange membrane	II	Teviron-B	1.46	0.190	3.0	0.91
			1.35	0.185	3.3	0.92
			1.26	0.185	3.1	0.92
			1.17	0.180	3.4	0.91
			1.12	0.180	3.2	0.92

Composition of the paste I: R/PVC=2.5, DVB/R=0.10, DOP/PVC=0.15, BPO/R=0.005.
Composition of the paste II: R/PVC=1.8, MVP/R=0.80, DVB/R=0.04, DOP/PVC=0.30, BPO/R=0.01.

Table IV shows the properties of the reinforcing materials under consideration. It was apparent that the poly(vinyl chlroide) cloth was advisable for a cation exchange membrane, and the poly(vinyl chloride) cloth, the polypropylene cloth, and the poly(ethylene terephthalate) cloth, for an anion exchange membrane. Subsequent experiments were, therefore, carried out with the poly(vinyl chloride) cloth, Teviron-A 0.13 mm. thick and Teviron-B 0.09 mm. thick, from the Teijin Co., Ltd.

Covering Material.—With a view of separating the layers of the paste coated onto the reinforcing material, the covering material was wound up simultaneously in layers.

A poly(vinyl alcohol) film (Kurarebiniron film from the Kurashiki Rayon Co., Ltd.) was adopted on the basis of its mechanical strength, flexibility, and lesser adhesiveness with the paste.

The Conditions of the Coating. — It was required that the paste should be coated uniformly in thickness and in composition, without a pinhole. The weight ratio of the paste to the reinforcing material (Resin ratio) was found to be closely connected with the requirements described above. When the resin ratio was too high (type H), the base membrane was likely to lack uniformity and the ion exchange membrane was apt to be uneven in its plane and the resinous part was apt to come off from the reinforcing material during the after-treatments. When the resin ratio was too low (type L), the ion exchange membrane was likely to have pinholes.

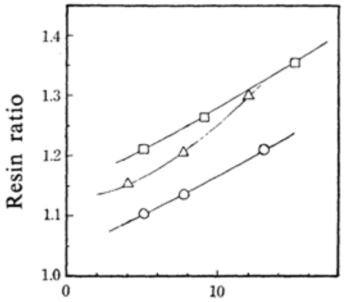

Fig. 2. Conditions of the coating—viscosity of the paste.
○ Paste I, Teviron-A
△ Paste I, Teviron-B
□ Paste II, Teviron-B
Pressure of the press roll is 80 kg. per a meter of the roll. Tension offered to the reinforcing material in length is 57 kg. per a meter of the reinforcing material in width. Rate of the coating is 1.36 m./min. Viscosity was measured with a viscosimeter from the Rion Co., Ltd.

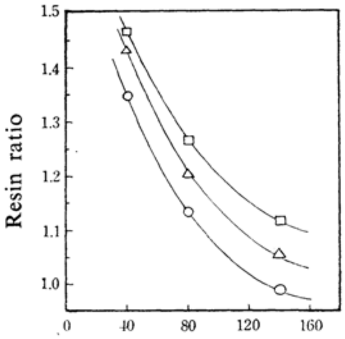

Fig. 3. Condition of the coating—pressure of the press roll.
○ Paste I, Teviron-A, Viscosity of the paste is 7 poise
△ Paste I, Teviron-B, Viscosity of the paste is 7 poise
□ Paste II, Teviron-B, Viscosity of the paste is 9 poise
Tension offered to the reinforcing material in length is 57 kg. per a meter of the reinforcing material in width. Rate of the coating is 1.36 m./min.

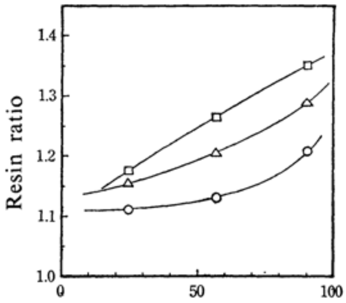

Fig. 4. Conditions of the coating—tension offered to the reinforcing material in length.
○ Paste I, Teviron-A, Viscosity of the paste is 7 poise
△ Paste I, Teviron-B, Viscosity of the paste is 7 poise
□ Paste II, Teviron-B, Viscosity of the paste is 9 poise
Pressure of the press roll is 80 kg. per a meter of the roll. Rate of the coating is 1.36 m./min.

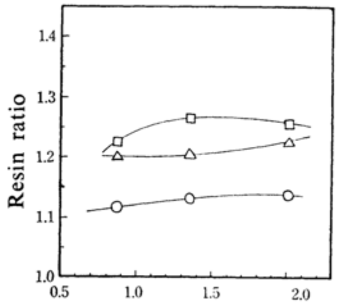

Fig. 5. Conditions of the coating—rate of the coating.
○ Paste I, Teviron-A, Viscosity of the paste is 7 poise
△ Paste I, Teviron-B, Viscosity of the paste is 7 poise
□ Paste II, Teviron-B, Viscosity of the paste is 9 poise
Pressure of the press roll is 80 kg. per a meter of the roll. Tension offered to the reinforcing material in length is 57 kg. per a meter of the reinforcing material in width.

Table V shows, however, that, as far as this study could ascertain, a resin ratio does not affect the electrochemical properties of the ion exchange membrane.

Judging from the mechanical properties and the appearance of the ion exchange membrane, the resin ratios of 1.12—1.17 for Teviron-A and 1.20—1.25 for Teviron-B were found to be most desirable (type M).

Figures 2—5 show the relations between the resin ratios and the conditions of the coating, i. e., the viscosity of the paste, the pressure of the press roll, the tension of the reinforcing material, and the rate of the coating.

With a paste with a high viscosity, the product is likely to be type H, and vice versa (Fig. 2).

When the pressure of the press roll is too high or low, the base membrane is apt to be type L or H (Fig. 3).

When increasing tension is offered to the reinforcing material, the resin ratio of the base membrane is increased (Fig. 4).

The rate of the coating did not affect the resin ratio, as is shown in Fig. 5, but when it was too high, the base membrane was apt to lack uniformity in its thickness. Considering the balances among the factors described above, the conditions of Table VI are recommended for the coating process.

TABLE VI. OPTIMUM CONDITIONS OF THE COATING PROCESS

Paste	I	II
Reinforcing material	Teviron-A or B	Teviron-A or B
Viscosity of the paste, poise	8	10
Temperature of the paste at the coating, °C	20	20
Pressure of the press roll (kg./m. of roll)	80	80
Tension offered to the reinforcing material in length (kg./m. of the reinforcing material in width)	50	50
Rate of the coating, m./min.	2	2

The Conditions of the Heating.—When the paste was heated, fine particles of poly(vinyl chloride) were fused to form a continuous film, in which the monomers were polymerized simultaneously, and part of the monomers were immersed and polymerized in the reinforcing material.

Because the fine particles of the poly(vinyl chloride) were swollen with the monomers, its fusion was carried out at comparatively low temperatures; i. e., the heating of paste I at 90°C and of paste II at 70°C were found to be sufficient to obtain a continuous film.

The temperature of the first heating, as well as the concentration of the catalyst in the paste, affected the characteristics of the products.

Table VII shows the effects of the temperature of the first heating. With a rising temperature the strengths of the base membrane and of the ion exchange membrane were decreased, and the expansion by the after-treatment was increased. These effects may be attributed to the fact that the more a monomer is immersed and polymerized in the reinforcing material with a rising temperature, the more the mechanical strength and the dimensional stability of the reinforcing material is decreased because of the polymer composed in it.

The effects of an increasing concentration of the catalyst were the reverse of those of a rising temperature, as Table VIII shows. This is accounted for by the fact that the increasing rate of the polymerization of the monomer, accompanied by the increasing concentration of the catalyst, may exceed the immersion rate of the monomers into the reinforcing material and so lead to a decrease in the polymer content in the reinforcing material; therefore, the strength of the reinforcing material does not decrease very much.

The Characteristics of Typical Ion Exchange Membranes.—The characteristics of typical ion exchange membranes obtained by the paste

TABLE VII. TEMPERATURE OF THE FIRST HEATING—PROPERTIES OF THE BASE MEMBRANES AND THE ION EXCHANGE MEMBRANES

	Cation exchange membrane						Anion exchange membrane						
Paste*[1]	I						II						
Reinforcing material	Teviron-A						Teviron-B						
Temperature of the first heating, °C	102	108	118	132	142	150	64	77	88	102	114	135	149
Burst strength of the base membrane, kg./cm²	7.1	6.5	5.5	5.0	1.8	1.8	5.0	4.8	4.7	3.4	3.2	3.0	3.1
Expansion by the after-treatment*[2]	1.10	1.11	1.12	1.12	1.13	1.13	1.03	1.03	1.04	1.04	1.05	1.05	1.06
Ion exchange membrane													
Burst strength, kg./cm²	3.9	3.7	3.3	2.8	3.0	2.8	4.9	4.4	4.0	3.4	3.6	3.0	3.4
Electric resistance, Ω·cm²	2.2	2.0	1.9	2.0	2.1	2.0	3.4	3.0	3.1	3.0	3.2	3.0	3.4
Transport number	0.87	0.87	0.86	0.86	0.85	0.86	0.86	0.90	0.91	0.91	0.92	0.92	0.90

*[1] Compositions of the pastes I and II: see Table I.
*[2] Conditions of the after-treatment: see Table II.

TABLE VIII. CONCENTRATIONS OF THE CATALYST—PROPERTIES OF THE BASE MEMBRANES AND THE ION EXCHANGE MEMBRANES

		Cation exchange membrane					Anion exchage membrane		
Paste[*1]		I					II		
Reinforcing material		Teviron-A					Teviron-B		
BPO/R (by weight)		0.001	0.005	0.010	0.020	0.030	0.015	0.040	0.060
Burst strength of the base membrane, kg./cm^2		2.6	5.5	6.7	7.3	7.5	4.7	5.1	5.0
Expansion by the after-treatment[*2]		—	1.12	1.11	1.10	1.09	1.04	1.02	1.01
Ion exchange membrane	Burst strength, kg./cm^2	—	3.3	4.0	4.0	4.2	4.0	5.0	5.1
	Electric resistance, $\Omega\cdot$cm^2	2.6	1.9	2.1	2.0	2.0	3.1	3.7	4.4
	Transport number	0.84	0.86	0.87	0.86	0.86	0.91	0.92	0.91

[*1] Compositions of the pastes I and II: see Table I except BPO.

[*2] Conditions of the after-treatment: see Table II. Temperature of the first heating was 120°C for paste I and 90°C for paste II.

TABLE IX. CHARACTERISTICS OF THE ION EXCHANGE MEMBRANES BY THE PASTE METHOD

Name	Type	Thickness mm.	Water content[*1]	Exchange capacity[*2]	Electric resistance $\Omega\cdot$cm^2	Transport number[*3]	Burst strength kg./cm^2
CL—2.5T	Cation exchange	0.15—0.17	0.30—0.40	1.5—2.0	2.8—3.3	0.98	3—4
CH—4	Cation exchange	0.20—0.22	0.30—0.35	2.0—2.5	2.3—2.7	0.97	3—4
AV—4T	Anion exchange	0.14—0.16	0.20—0.30	1.5—2.0	3.0—4.0	0.98	6—7
AVS—4T	Anion exchange	0.15—0.17	0.25—0.35	1.5—2.0	3.7—4.7	0.98	4—6

[*1] Equilibrated with 0.5 N sodium chloride aqueous solution, [g. H_2O/g. Na-form dry membrane (or Cl-form)].

[*2] [meq./g. Na-form dry membrane (or Cl-form)].

[*3] Measured by electrophoresis with 0.5 N sodium chloride aqueous solution, current density: 10(mamp./cm^2), at 25°C.

method using the roll-coating system are shown in Table IX.

The CL and CH types are cation exchange membranes, and the AV and AVS types are anion exchange membranes; the AVS type especially has much less permselectivity for SO_4^{2-} than Cl^-.3) The transport numbers in the ninth column were measured by the electrophoresis described in a previous paper.4)

According to the results obtained by the electrophoretic concentration of sea water over a long period,3) the ion exchange membranes obtained by the paste method were proved to have a good durability.

Summary

A method for the preparation of ion exchange membranes called the "paste method" has been developed into a semicontinuous preparation.

The roll-coating system being employed, a base membrane 1 m. wide and 50 m. long is prepared continuously; the ion exchange group is then introduced to it.

The ion exchange membranes thus prepared have been proved to have excellent electrochemical and mechanical properties as well as an excellent appearance.

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3) R. Yamane, Y. Mizutani, H. Motomura and R. Izuo, *J. Electrochem. Soc. Japan* (*Denki-Kagaku*), **32**, 277 (1964).

4) R. Yamane, ibid., **31**, 240 (1963).