Making of Diaphragms and Measurements of their Permeabilities and Electrolytic Resistances for the Na₂SO₄ Electrolysis. —Especially about the Micro-porous Rubber Diaphragm—

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A number of demands, contradicting each other, must be satisfied on the filter diaphragm material for the electrolysis of sodium sulfate solution. The diaphragm has to be resistant to the electrolytic product, to sulfuric acid on anode side and to oxygen and ozone produced by the anode process. More important demands are the suitable permeability and the low electrolytic resistance caused by the length, width and the numbers of pores and also by the ability to be wetted and the electrophoretic behaviour⁽⁷⁾ of the filter diaphragm. The other ones are the resistance against heat, good reproducibility of permeability, mechanical strength and so on.

The purpose of this report is to find the most suitable filter diaphragm materials which have good capillary and electrochemical properties for the electrolysis of sodium sulfate solution. Unfortunately, there is no diaphragm which satisfies, with only one material, a number of demands altogether as described above.

Table 1 shows the characteristic of typical membranes. The blue asbestos cloth has good resistance to sulfuric acid, oxygen and ozone as shown in Table 2, but is too permeable and not good in the cell. The problem is to have such a low permeability that the sulfuric acid formed at the anode will not be excessively diluted by large quantities of sulfate solution.

Table 1 Characteristics of Typical Membranes.

Characteristic	Membranes treated on and in vinylon cloth			PVCi microporous sheet	Blue asbestos cloth	White asbestos cloth	Ebonite microporous sheet (for Lead Accumulator)
	by PVCi	by Natural Latex	by Synthetic Rubber				
For ozone and oxygen*	△	×	×	○	⊙	×	×
For H ₂ SO ₄ (0-20%, 50°C)	○	○	○	○	⊙	×	⊙
For heat (50-70°C)	×	○	○	×	○	○	○
Electrochemical** property	×	⊙	⊙	×	△(×)	△(×)	×
Reproducibility of permeability	×	○	⊙	△	△(×)	△(×)	△
Mechanical strength	○	○	○	△	○	○	×

* Durability against Oxidation.

** Selective permeability of sulfate and sodium ion⁽⁸⁾.

Table 2 Attack of H₂SO₄ and Ozone on Blue Asbestos Cloth in Stationary, 250 g/l H₂SO₄ Anolyte and 10 Amp/dm², 45°-55°C.

Elect. Exp. No. 45.			Elect. Exp. No. 46'			
No.	Fe in anolyte ^{(1),(2)} (mg/l)	Concentration of H ₂ SO ₄ (g/l)	No.	Fe in anolyte (mg/l)	Concentration of H ₂ SO ₄ (g/l)	Ozone ⁽³⁾ in anolyte (mg/l)
45-3-2-11	7.7	245.0	46-6-288	17.4	257.9	687.6
" -19	11.0	255.0	" - 91	9.9	259.9	582.5
" - 3	10.1	251.0	" - 68	14.0	257.0	493.2
" - 7	11.8	250.0				

* Studies on the Electrolysis of Sodium Sulfate Solution (Part. 2).

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Further, at low permeability, the rate of flow must still be so great in the pores that the H^+ will be prevented from migration out of the anode compartment. Therefore, the length, number and width of pores must be as uniform as possible. The pores must be so narrow that the gaseous electrolytic products cannot mix with one another.

The microporous rubber sheets which are formed on and in the suitable synthetic fiber cloth (for example, Vinylon cloth), were so satisfactory with regard to permeability and reproducibility during electrolysis, that this material was used exclusively in later experiments. But this material cannot sufficiently endure the attack of anodic ozone and sulfuric acid; the rubber sheet is ozonized slowly, darkened especially at the part of the upper surface of anolyte and finally is broken and is not applicable for long time use.

Therefore, in practical operation, as calculated from Eqs. (2) and (3), We chose the combined diaphragm which consists of blue asbestos cloth and rubber diaphragm and in which the former faces the anode side and the latter is placed behind the former. This combined diaphragm has a long life time (about 3 years) and produces high concentration of sulfuric acid and its high current efficiency.

Next, the various micro-porous rubber diaphragms are made and their permeabilities and electrolytic resistances are tested. As the substrate, we use the Vinylon thick clothes of 40-60 Vol-% space. The natural latex is ozonized more easily than synthetic rubber, such as Hycal OR-S, Bunna S, GR-M, Neopren, GR-I, Thiokol A and so on. Hycar OR-15 is the most durable among them. Powdered Sulfur (as vulcanizer), starch, inorganic salt (MgO, ZnO etc.) (as pore forming agents), vulcanizing accelerator, antioxidant and other materials⁽⁸⁾ are suspended in the solution of Hycar OR-15 in benzen.

The suspension is painted and padded homogeneously all over and throughout the fiber cloth over several times, and then it is vulcanized under saturated water vapor at 100-1130°C, Ca. 4 hr. and washed with hot 5% sulfuric acid. According to this operation, the suitable rubber diaphragm for the cell is obtained. The number (10^6 - 10^7 per square cm) and radius of pores (1 - 10μ)^{(6), (9), (10)} are calculated from permeability using Eq. (4) and (5). These results are summarized in Table 3.

Fig. 1 is the apparatus for measuring electrolytic resistance of diaphragm, which is provided with voltage electrodes and current electrodes, respectively, to avoid the overvoltage of current electrodes.

Table 3 Numbers and Radius of Pore in Diaphragm.

Diaphragm	Porosity q	Permeability k_c	Distortion factor α	No. of Pore n (Nos./ $\times 10^{-6}$ cm^2)	Radius of pore r (μ)	Remarks
Blue asbestos cloth	0.50	0.24	3.0 ^{(10), (11), (12)}	4.88	1.806	—
Micro-porous Pvc sheet	0.80	2.30	3.0	1.30	4.43	—
Vynlon cloth treated with Hycar OR-15	0.30	0.70	3.0	0.47	4.52	Elect. Exp. No. 39 d=0.5 mm
"	0.60	0.07	3.0	2.41	0.89	Piece of test sample d=1.0 mm
Ceramic diaphragm QN-1	0.408	0.051	2.8	16	0.888	Lit., (9)
" QN-201	0.429	0.022	2.6	45	0.549	"
" B-25	0.243	0.004	3.2	65	0.345	"
Canadian asbestos paper cloth	0.600	0.025	2.2	57	0.468	"

- ① Electrode of direct current source; $70 \times 70 \times 1$ mm Pb plate
 ② Electrode for voltage measurement; $5 \text{ mm } \phi$ pure Cd rod
 ③ Lead accumulator; $2 \text{ V} \times 3$
 ④ Variable resistance; 10Ω , $3 \sim 5 \text{ A}$
 ⑤ Ammeter; Calibrated max 1.5 , 5 A
 ⑥ Voltmeter; Inner resistance 3000Ω , 3 V
 ⑦ Sample; Membrane area 20 cm^2
 ⑧ Cell; Transparent acrylic resin $160 \times 80 \times 70 \text{ mm}$

Fig. 1 Measuring Apparatus of the Electrolytic Resistance of Membranes.

Table 4 Permeabilities and Electrical Resistances of Main Membranes.

Membranes	Thick- ness (mm)	Per- mea- bility k_c	Electrical Resistance			Membranes	Thick- ness (mm)	Per- mea- bility k_c (before electro- lysis)	Electrical resistance			Per- mea- bility k_c (after electro- lysis)
			Ω /20 cm ² / 1 Sheet		Ω /dm ² /mm 25°C				Ω /20 cm ² / 1 Sheet		Ω /dm ² /mm 25°C	
			25°C	50°C					25°C	50°C		
PVCl Micro-Porous Plate	1.2	2.31	0.045	0.670	0.0075	Hycar OR-15 Treated on Vinylon Serge	0.5~0.6	0.561	0.061	0.065	0.02	—
Blue Asbestos Cloth	2.1	0.218	0.014	0.0075	0.0013	Natural Latex Treated on Vinylon Serge	0.5~0.6	nearly 0	0.20	—	0.067	—
Ebonite Micro- porous Plate	0.5	nearly 0	0.193	0.03	0.077							
”	0.8	0.136	0.015	0.01	0.00375	Elect. Exp. No. 13	1.6	—	0.205	0.105	0.026	1.25
Vinylon cloth Broad	0.3	2.58	0.009	0.0066	0.006	” No. 16	1.25	—	0.12	0.075	0.019	0.675
Vinylon cloth Serge	0.43	—	0.007	0.0025	0.0032	” No. 17	1.3	—	0.38	0.255	0.066	0.208
Vinylon Cloth Serge (coarse)	0.44	—	0.0063	0.0025	0.0029	” No. 25	1.3	0.26	0.405	0.18	0.062	0.39
Vinylon cloth Canvas No. 11	0.55	3.33	0.017	0.0075	0.0062	” No. 30	1.35	0.162	0.145	0.075	0.022	0.162
Vinylon cloth coarse cloth S-25	0.42	Ca 13.9	0.007	0.0044	0.0033	” No. 35	1.3		0.08	0.07	0.012	1.42
Vinylon cloth Thick and Twilled No. 0	1.3	70.90	0.032	0.017	0.0044	” No. 38	1.0		0.271	—	0.054	4.59
Vinylon cloth Thick and Twilled No. 18	1.3	14.20	0.025	0.016	0.0038	” No. 39	1.0		1.17	0.30	0.234	0.72
Filter cloth	0.8	4.00	0.901	0.06	0.225							

Its apparatus contains the mixture of $250 \text{ g/l H}_2\text{SO}_4$ and $210 \text{ g/l Na}_2\text{SO}_4$. The current is kept constantly at 1.0 Amp. during the measurement. Table 4, Fig. 2 show the electrolytic resistances and permeabilities of various membranes, which are measured as described above.

Fig.2 Electrolytic resistance

Fig. 2 shows the electrolytic resistance of main membranes, and its upper part represents the relations between the thickness of diaphragm itself (mm.) and resistance ($\Omega/\text{dm}^2/\text{l sheet}$), while its lower part shows their electrolytic resistances per 1 mm. thickness. The plots of the same diaphragm are connected by straight line respectively.

Conclusion : We sought and tested the suitable diaphragm material for the electrolysis of sodium sulfate solution, but none of them, made of only one sort of material, was satisfactory.

(1) We choose the combined diaphragm which consisted of blue asbestos cloth faced to the anode side and micro-porous diaphragm put behind the asbestos cloth. The combined diaphragm of this type was suitable for the cell both theoretically and practically. During the long period of operation, its diaphragm gave the good results of electrolysis constantly. The reasons are as follows : the blue asbestos are excellent in the durability against H_2SO_4 or ozone, and the rubber diaphragm keeps the pores electrochemically good.

(2) The micro-porous rubber diaphragm, which formed on and in the suitable synthetic fiber cloth as substrate (for example, Vinylon cloth), was made by proper vulcanization of natural latex or synthetic rubber. The radius of pores are $1-10 \mu$, the numbers of pores are 10^6-10^7 per square cm.

(3) Rubber diaphragm thus made has good reproducibility of permeability and electrolytic resistance and it is the indispensable component of material of diaphragm in practical electrolysis of sodium sulfate solution.

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