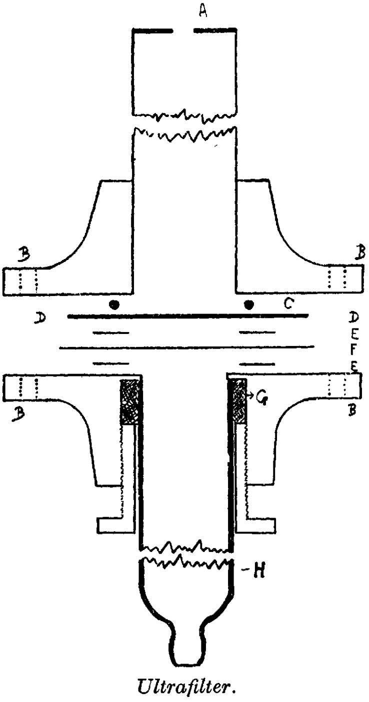
CXLVI.—*Preparation of Nickel Membranes for Ultrafiltration.*

By John Manning.

The membranes which have hitherto been used for ultrafiltration have usually been prepared by impregnating filter-papers with nitrocellulose dissolved in acetic acid or in a mixture of ether and alcohol. They can neither be used at high temperatures nor with solvents such as acetone. In this communication are described membranes, prepared by the electrical deposition of nickel on fine nickel gauze, which can be used at high temperatures and in the presence of organic solvents.

The apparatus shown in the figure is made of nickel-plated phosphor-bronze. The two flanges are bolted together with the membrane between. The membrane alone could not stand the high pressure involved and was therefore supported by a nickel disc through which several holes had been drilled. Various materials were tried as washers, but the most suitable was a pure silver-wire ring softened by annealing. This was flattened between the flanges when they were screwed together and made a very satisfactory joint. The apparatus could be used with pressures up to sixteen atmospheres.



Ultrafilter.

A *Screw for pressure gauge.* B *Holes for 4⅜″ bolts.* C *Silver ring.* D *Membrane.* E *Silver washers.* F *Perforated nickel support for membrane.* G *Asbestos compressed against glass tube.* H *Thick glass tube.*

As a foundation for the membrane, fine nickel gauze (mesh 200) and, in later experiments, phosphor-bronze gauze was used.

In the early work, a nickel sheet of suitable size was made the anode in a solution which was agitated by using the cathode itself as a vertical stirrer. The solutions were similar to those used for ordinary nickel-plating, containing, for example, 120 g. of nickel sulphate, 22·5 g. of ammonium chloride, and 15 g. of boric acid per litre. With the current densities first used, smooth, even, and hard deposits were obtained, perforated with small holes. If the plating process was continued until these were filled in, the rest of the membrane became entirely impermeable. With high current densities, *i.e.*, 2 amps. per 4 sq. in., at 3·3 volts very irregular deposits were obtained. As the current density and *E.M.F.* were decreased, the character of the deposit changed; it became less hard and darkened in colour and, at 0·3—0·5 amp. per 4 sq. in. at 0·9—1·1 volts, the resulting membranes were almost black and fairly regular. The suitability of the above membranes for ultrafiltration was tested by means of the following experiments.

A colloidal solution of silver in stearic acid, prepared by the reduction of silver stearate suspended in the acid (Giles and Salmon, J., 1923, **123**, 1600), was filtered at 140° under a pressure of 2 atmospheres. Perfectly clear stearic acid came through, the colloidal metal being entirely retained as a blue deposit on the membrane. A second experiment was carried out with a solution in which only partial reduction had taken place, so that there was present a considerable excess of silver stearate. In this case, silver was found in the filtrate, which was colourless, showing that, although the colloidal metal had been retained, the silver stearate, which we believe to exist as simple molecules, passed through the membrane.

These membranes would also successfully filter arsenic sulphide and ferric hydroxide hydrosols, but they were not satisfactory with solvated organic colloids, such as gelatin in water, or nitrocellulose in ether and alcohol. It seemed probable that filtration was taking place through a small number of holes, whilst the rest of the membrane was practically solid. These holes, which would retain inorganic solids and permit the passage of the solvent, became rapidly blocked up with gelatin. It was therefore necessary to obtain a more porous and open deposit, and experiments were carried out to determine the effect of changes in the composition of the plating bath on the character of the deposit.

The presence of nickel chloride is usually considered to give a soft deposit; consequently, membranes were prepared by plating in solutions of that salt (100 g. of nickel chloride, 20 c.c. of concentrated hydrochloric acid, and 1500 c.c. of water), hydrochloric acid being added to give a continuous evolution of gas at the cathode and thus increase the porosity of the deposit. At low current densities, the membranes were more smooth and even than with higher current densities, but contained green patches due to the high concentration of chlorine ions present; consequently, in later experiments, sulphuric acid was used instead of hydrochloric acid, and nickel sulphate was substituted for a part of the chloride. Table I shows the effect of varying the relative proportion of chloride and sulphate in the plating bath, the most effective membranes being obtained when the ratio of sulphate to chloride was 50 to 80.

The effect of varying the hydrogen-ion concentration on the nature of the membrane was also investigated. In one experiment, boric acid was used instead of sulphuric acid, in the hope that it would act as a hydrogen-ion regulator. Deposits in this case were hard with bright streaks and not efficient for filtration. In later experiments, the following plating mixture was used: 100 g. of nickel sulphate, 80 g. of nickel chloride, 20 g. of sodium acetate ($3H_2O$), and 1500 g. of water. The membranes which were obtained were suitable for ultrafiltration and were much less brittle than those prepared from previous solutions. With a still larger proportion of acetate the membranes became greenish and

TABLE I.

The bath contained 1500 c.c. of water, 5 c.c. of concentrated sulphuric acid, and weights (g.) of nickel chloride and sulphate as indicated.

Current densities: 1·1 amps. down to 0·4 amp. per 4 sq. in. Potential difference: 3·5 volts for 1 hr. and 2 volts for about 18 hrs.

Bath.		Remarks on membranes.		
$NiSO_4$.	$NiCl_2$.	Appearance.	Thickness.	Filters
0	100	Black.	Flimsy.	Night blue.
20	100	Greenish.	Denser.	,,
40	80	,,	,,	Night blue and gelatin.
50*	80	Brown, sometimes greenish.	,,	Night blue and cellulose acetate.
120	20	Irregular.		
120	0	No deposit from acidified solutions.		

* The 3rd and 4th membranes prepared from this bath were much better than the first two. The bath was filtered and acidified with 5 c.c. of concentrated sulphuric acid before each successive plating operation.

still more pliable. In the next paragraph are described experiments carried out with these membranes.

Ultrafiltration of Cellulose Acetate in Acetone and Water.—Cellulose acetate was dried and dissolved in a mixture of acetone and water, the acetone having been purified by the method of Werner and Shipsey (J., 1913, **103**, 1255). Solutions of known concentration were prepared in tightly-corked flasks and, to prevent evaporation, were transferred to the ultrafilter through glass tubing. The filtration of 3 to 5 c.c. took from 10—15 hrs. at a pressure of 10—14 atmospheres and, to avoid loss of acetone by evaporation, the filtrate was allowed to fall directly into a known weight of water. The acetone was estimated by Messenger's method (*Ber.*, 1888, **21**, 3386). The results of three experiments are shown in Table II, the figures in the column " Cellulose acetate " showing the weight (g.) added to 100 g. of mixed acetone and water.

TABLE II.

Initial concentrations.			Concentrations after ultrafiltration.	
Cellulose acetate.	Acetone %.	Water %.	Acetone %.	Water % (by diff.).
3·25	74·9	25·1	75·5	24·5
5·41	68·0	32·0	68·3	31·7
3·73	71·1	28·9	71·7	28·3

The analytical error is about 1%.

The concentration of the acetone would be expected to fall on account of its volatility, but, on the other hand, there appears to be a slight increase in concentration in the filtrate, indicating apparently that water is taken up by cellulose acetate (from these mixtures, at any rate) to a greater extent than acetone.

Ultrafiltration of Sodium Stearate.—Solutions of sodium stearate of concentrations lying between $N/2$ and $N/6$ were ultrafiltered at a temperature between 80° and 90°, the whole ultrafilter being surrounded by an electric oven. In every case, only a negligible amount of stearic acid penetrated the membrane, whilst the alkalinity of the filtrate was always less than $0{\cdot}01N$, indicating that membrane hydrolysis had not taken place to any considerable extent.

Solutions of casein and gelatin were also successfully filtered by means of this membrane. In the case of 0·5% gelatin sols, extremely small quantities of gelatin passed through the filter at 16°, but, on raising the temperature to 45°, the gelatin almost entirely passed through. This means that the particles present at the higher temperature are too small to be retained. If we accept the view, which will be discussed in a later communication, that the difference between gelatin at these two temperatures is due to the secondary linking up of particles, then the primary particles of gelatin are considerably smaller than is usually believed.

Determination of Size of Pores.—One of Bechhold's methods for the determination of the size of pores depends on the minimum air pressure which will produce bubbles through the membrane covered 1 mm. deep with water.

Some irregularities in the membranes were detected by this method, one or two large holes usually being found. In a particular case, at a pressure of 3·5 atmospheres there was bubbling at one hole, at 4 atmospheres at 5 holes, and at 4·8 atmospheres the bubbling became general. In view of the results obtained, it seems probable that these large holes are very quickly blocked up during filtration. It was observed many times that initially the colloid came through, but was retained after the first few drops.

The finest membranes obtained contained pores of between 50—80 $\mu\mu$, the size increasing as the nickel sulphate content of the plating bath increased, until the average size of the pores was 300 $\mu\mu$, for a bath containing 90 g. of nickel sulphate, 80 g. of nickel chloride, 1500 g. of water, and 5 c.c. of concentrated sulphuric acid.

Summary.

Membranes have been prepared by nickel plating on bronze or nickel gauze which are capable of retaining most colloids on ultrafiltration. They can be used at high temperatures, and with

solvents which will attack the usual membranes. The average size of the pores can be controlled by varying the plating bath, so that they can be used for fractional filtration.

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