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The effect of an organic ion-exchange resin on properties of heterogeneous ion-exchange membranes

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ABSTRACT

This case study deals with relationships between characteristic properties of organic ion-exchange resins and heterogeneous ion-exchange membranes. At first chemical and temperature stability, humidity and particle size distribution of different types of ion-exchange resins was analyzed. Subsequently, membranes were prepared by using different filler/polymer matrix ratio or by using milled resins with different particle size distribution. Finally, different ion-exchange resins were used for preparing of heterogeneous ion-exchange membranes at fixed filler/polymer matrix ratio. We analyzed many characteristic properties of raw materials, intermediate and final products and we paid attention to process parameters during preparing of membranes too. It was proved that there are important relationships between properties of a membrane and the type of resin used for its preparation and the process of membrane preparation. The results show that most of ion-exchange resins can be used for ion-exchange membranes preparation but with different impact on characteristic properties of membranes. We also proved that increasing of filler/polymer matrix ratio or using very fine particle size distribution of milled resin improve electrochemical properties of membranes at the expense of worst mechanical properties and more complicated membrane preparation. On the basis of these results we are able to modify composition of heterogeneous ion-exchange membranes to reach required properties.

Keywords: Heterogeneous ion-exchange membrane; Membrane modification; Particle size of distribution

1. Introduction

1.1. What is the ion-exchange membrane?

The ion-exchange membrane is a special type of separation membrane which separates cations and anions from solution with high selectivity. The membrane has fixed ionic groups and free counter-ions which can be transported through the membrane. Co-ions cannot be transported or their transport is limited.

Generally two types of ion-exchange membranes exist: homogenous and heterogeneous. Heterogeneous ion-exchange membranes consist of four basic components: ion-exchange resin, polymer matrix, additive and fitting fabrics. Homogeneous ion-exchange membranes have only one basic component: functionalized polymer, but for increasing their strength fitting

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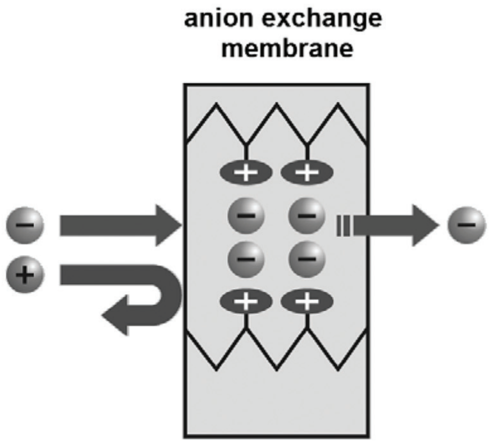

Fig. 1. Scheme of ion-exchange membrane.

fabrics are used too. Heterogeneous systems are more variable and complicated, but we can modify them more easily.

1.2. Using of ion-exchange membranes

These types of membrane are often used for electrodialysis, electrodeionization, membrane electrolysis and electrophoresis. All applications have special requirements on membranes according to their usage. Main parameters which are monitored are electric resistance, permselectivity, mechanical stability, ion exchange capacity, hydrodynamic permeability, chemical and temperature stability.

Ion-exchange membranes are stacked with a help of special spacer to form diluate and concentrate chambers. Under the electric field cations and anions are moving to opposite charged electrodes. Principle of separation is passing of cations through cation exchange membranes and anions through anion exchange membrane. Passing of ions through the opposite membrane is blocked (see Fig. 3).

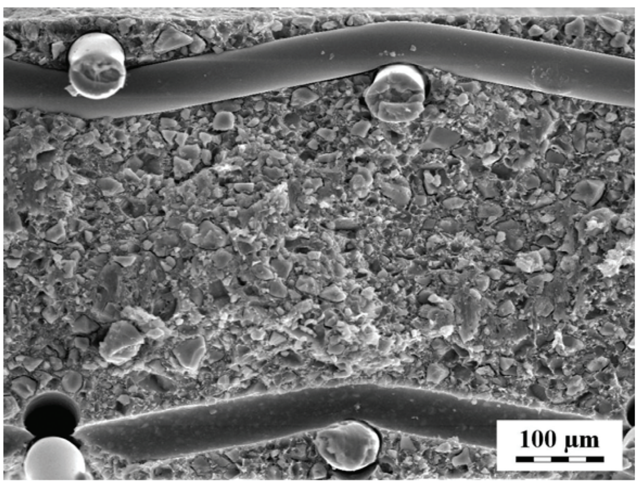

Fig. 2. Morphology of heterogeneous ion-exchange membrane RALEX.

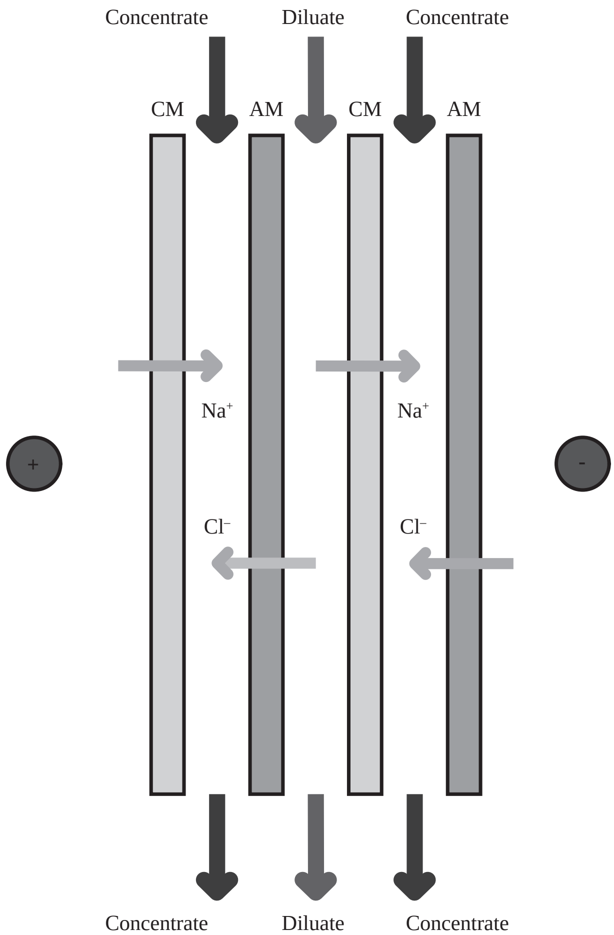

Fig. 3. Scheme of electrodialysis.

Table 1
Requirements of basic membrane properties dependence of technology

Membrane property/technology	Electrodialysis (ED)	Electrodeionization (EDI)	Electrophoresis
Low electrochemical resistance	Important	Can be higher	Can be higher
Low back diffusion	Can be higher	Important	Can be higher
high mechanical strength	Can be lower	Can be lower	Important

1.3. Reasons for modification and possibilities of modification

As it was mentioned above, there are many applications of ion-exchange membranes which require different operation conditions and membrane properties [1]. In the Table 1 there is a comparison of membrane properties requirements in three main technology applications of membranes. Differences in requirements can occur even within the same technology. For example electrodialysis of high concentrated solutions requires membranes with low electrochemical resistance, but tertiary treatment of low concentrated waste waters needs a long-term durable membrane with high current efficiency whereas low electrochemical resistance is not important.

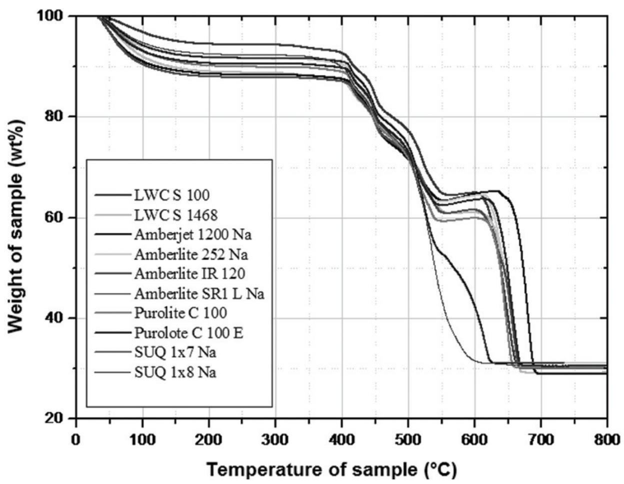

Fig. 4. TGA of cation exchange resins.

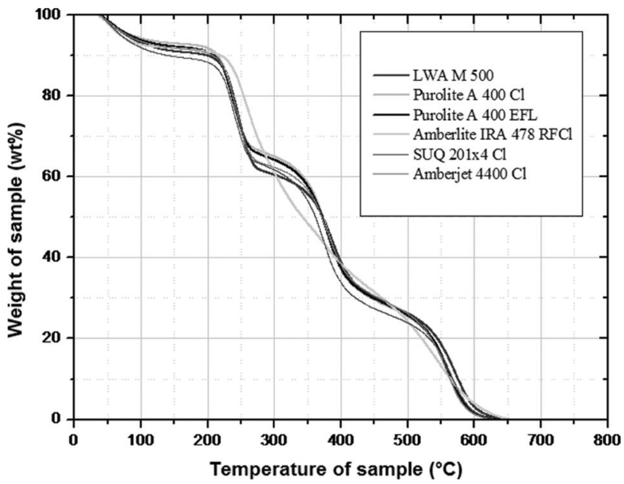

Fig. 5. TGA of anion exchange resins.

Therefore there is a need to modify characteristic membrane properties according to requirements of different applications.

Membrane properties of heterogeneous membranes depend on properties of raw materials (ion-exchanger, polymer matrix, additive and fitting fabric) and on the technology of preparation (e.g. particle size of milled resin, efficiency of homogenization of mixture of polymer matrix and ion-exchanger, concentration of ion-exchanger in the mixture) [2,3]. Our case study was aimed to understand relationships between characteristic properties of an ion-exchange resins, polymer matrix and heterogeneous ion-exchange membranes.

2. Results

2.1. Ion-exchange resin selection and characterization

At the first stage the temperature stability, humidity and particle size distribution of different type of ion-exchange resins was analyzed. We tested strong acid, strong, weak and strong/weak base ion-exchange resins of different internal structure (gel, macro porous, styrene-divinylbenzene, polyacrylate) and brand names.

We found out the most of anion exchange resins are thermally stable up to 150°C for about 60 min and about 10 min at 200°C. Cation exchange resins are more stable. Therefore polymer matrix with low melting point is needed for thermoplastic technique of preparation of heterogeneous ion-exchange membranes. Low density polyethylene is the most widely used and suitable type of polymers.

Due to high ion exchange capacity of tested ion-exchange resins, their humidity was very high; approximately from 40 to 70 weight %. Particle size distribution of resins depends on weather the resins are

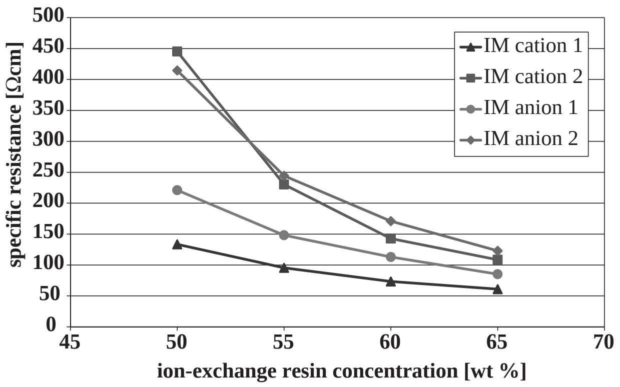

Fig. 6. Dependence of specific ionic resistance on concentration of ion-exchange resins.

sieved or not. Some of them have a narrow distribution called as monodisperse and some of them have particles from 0.3 to 1.2 mm. For properties of heterogeneous ion-exchange membranes this parameter is insignificant, because during membrane preparation procedure resins are milled to particles smaller than 0.1 mm (approximately 10–20 times smaller than original spherical particle).

2.2. *Effect of concentration of ion-exchange resin powder*

The different filler/polymer matrix ratio of milled resins was investigated. For preparation of ion-exchange powder industrial jet or vibrating mills were used. At first, small samples of composite and final membranes were prepared at laboratory equipment. Subsequently, industrial equipment was used to check the scale-up from laboratory to industrial scale.

We state the ion conductivity rapidly increases with ion-exchange content (see Fig. 6). We also state the ion conductivity depends on the type of ion-exchange resin (gel, macroporous, cross-linking, etc.).

High ion-exchange content enables more extensive swelling of membrane in contact with water. During the swelling the micro- and macroporosity increase. This mechanism is very important for membrane ion-conductivity. On the other side, high porosity decreases permselectivity.

The amount and size of pores depend on concentration and particle size of ion-exchange resin and also on preparation conditions. During the laboratory preparation of samples inhomogenity can occur. Therefore permselectivity of cation samples in Fig. 7 seems to be independent on ion-exchange content.

2.3. *Effect of particle size distribution of ion-exchange resin powder*

During the long term production of heterogeneous ion-exchange membranes we noticed changes of electrochemical parameters of membranes although the all parameters monitored during manufacture process (humidity of ion-exchange resin, time of milling, constant ion-exchange resin/polymer ratio etc.) were constant. We started to monitor particle size of milled resin by analyzer based on laser diffraction. During 1 year we noticed changes of particle size of ion-exchange powder. Therefore we prepared ion-exchange composites using ion-exchange powder with different particle size distribution at fixed ion-exchange resin/polymer ratio. Our first results were verified on different types of resins with the same results. Decreasing size of particles improves ion conductivity, but at the expense of decreasing mechanical properties, workability, permselectivity and also increasing cost of milling.

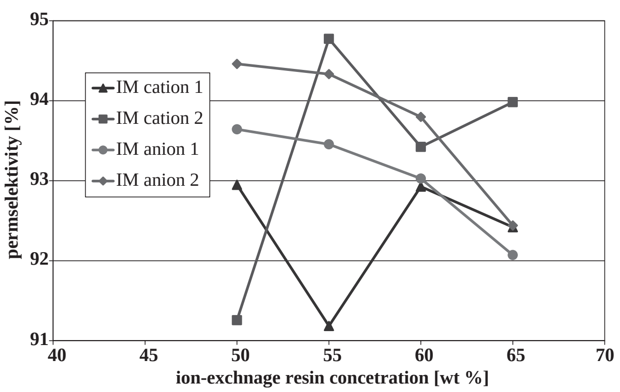

Fig. 7. Dependence of permselectivity on concentration of ion-exchange resins.

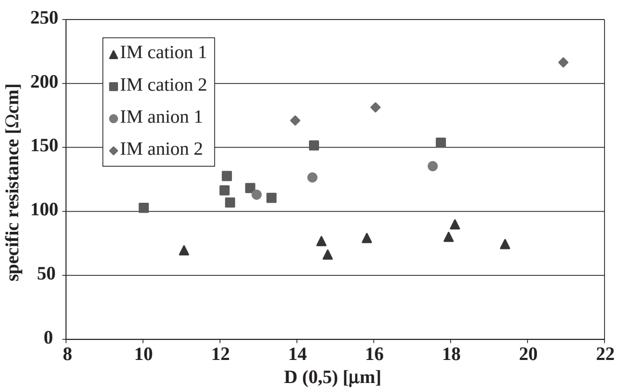

Fig. 8. Dependence of specific ionic resistance on particle size of ion-exchange resins defined as quantile D (0.5).

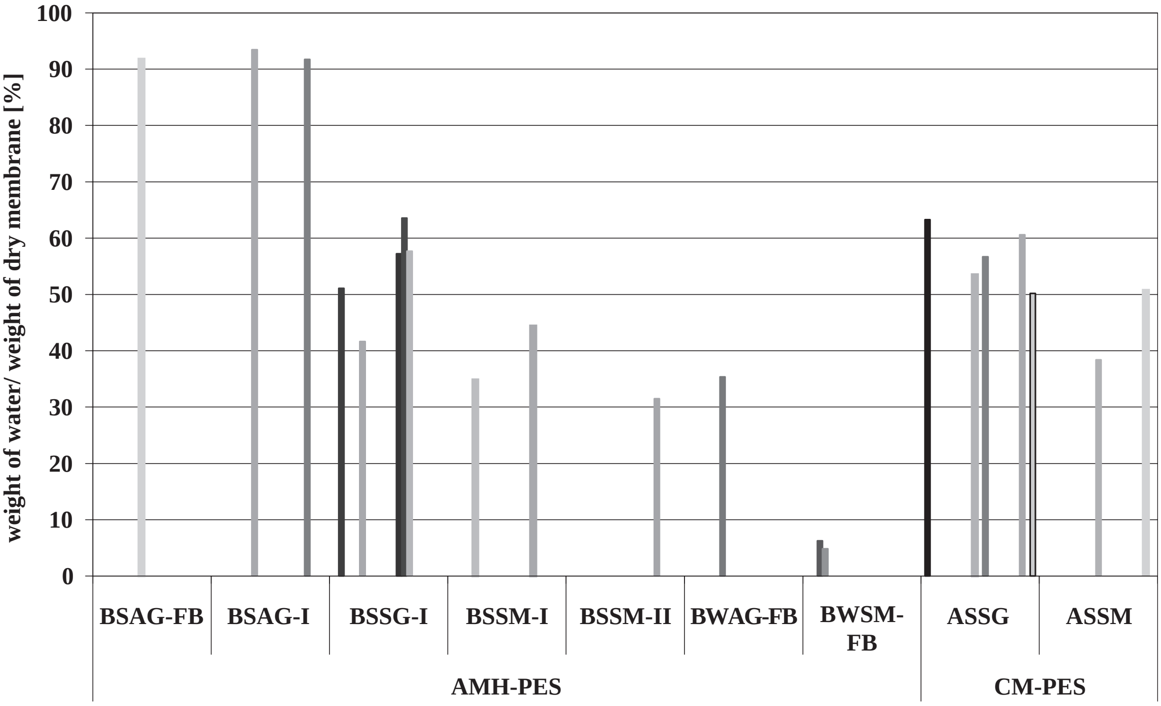

Fig. 9. Dependence of water swelling on type of ion-exchange resin.

2.4. Effect of ion-exchange resin type

At the final stage we prepared samples of membranes using different types of resins on constant conditions: humidity and particle size of dry resin, fixed resin/polymer ratio, temperature, time and pressure of lamination, etc. We observed important

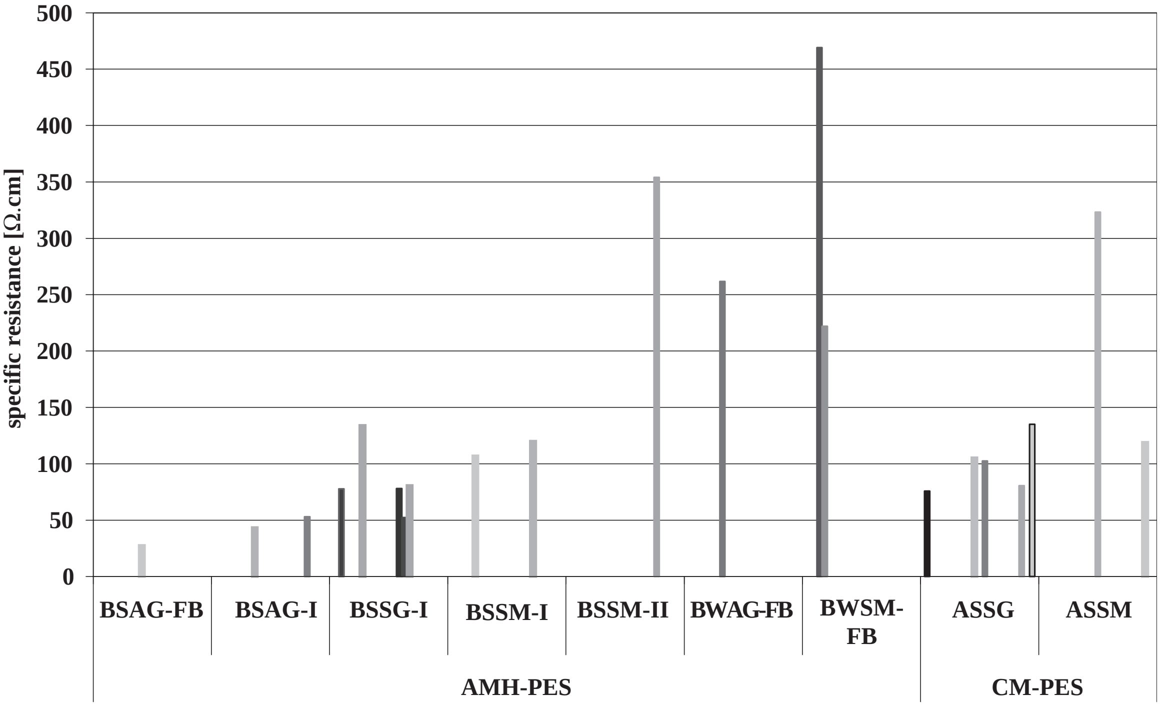

Fig. 10. Dependence of specific resistance on type of ion-exchange resin.

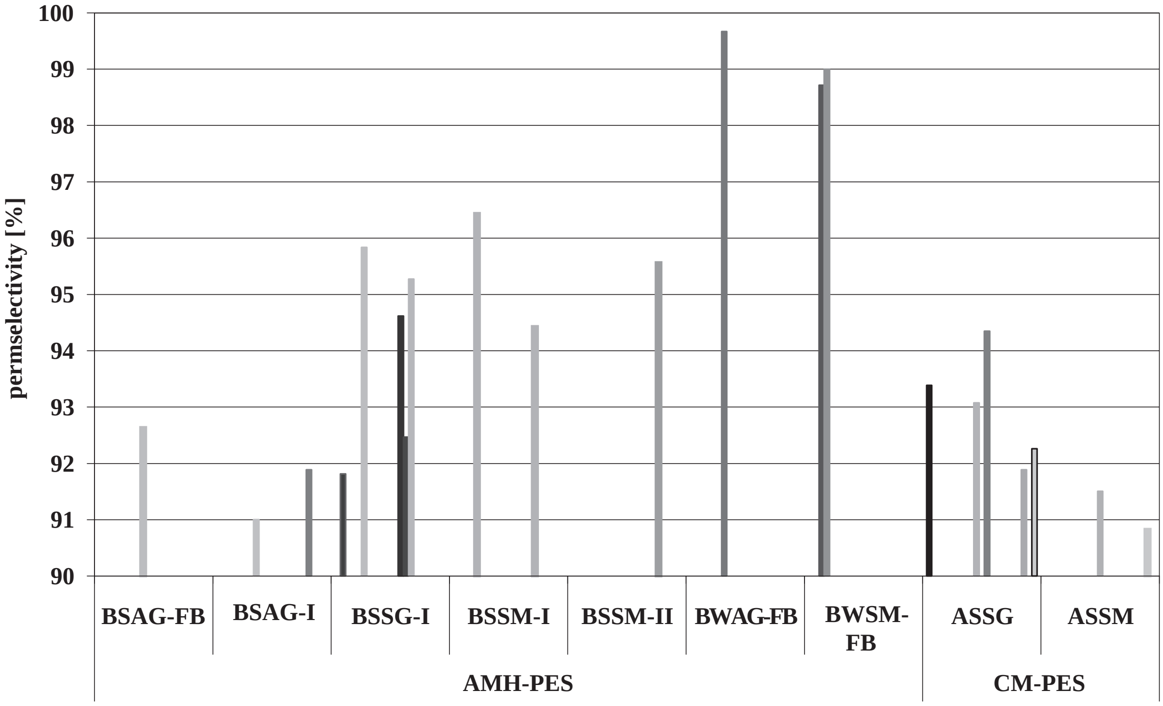

Fig. 11. Dependence of permselectivity on type of ion-exchange resin.

differences of characteristic properties in dependence on resin type. Acrylate based resins are more flexible and these resins swell more than styrene-divinylbenzene based resins. Therefore the acrylate based resins have best ion conductivity but worst permselectivity at the same resin/polymer ratio.

Weak base resin and generally all macroporous resins have worse electrochemical properties than gel type.

For heterogeneous ion-exchange membranes are suitable gel type of strong base or acid resin. Acrylate based resins can be also suitable but with lower resin/polymer ratio. This modification increases permselectivity at the expense of increasing ion resistance and mechanical stability during swelling. Although a smaller amount of dry resin is needed final costs are higher due to higher costs of this type of resins and higher water content.

3. Conclusion

- We state there is a strong dependence of ion-exchange concentration, particle size and resin type on characteristic properties of heterogeneous ion-exchange membrane.
- We confirm that the preparation technology has a significant effect on membrane morphology.
- We are able to modify the composition of membrane to reach appropriated characteristic properties according to technology demands.

Acknowledgments

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