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Cast and Reinforced Membranes from Aquivion® PFSA Dispersions

Aquivion® PFSA can be used to produce cast ion exchange membranes that offer the option of being mechanically reinforced with fibers, webs, fabrics, and other materials. Developers can actively influence film quality by using liquids tailored for specific coating equipment and by optimizing the thermal treatment sequence during line operations.

Typical Aquivion® PFSA Membrane Applications

- Polymer electrolyte fuel cells and water electrolyzers
- Redox flow batteries
- Water purification units
- Gas-to-gas or liquid-to-gas humidification systems

Product Selection

Aquivion® PFSA products carrying an S suffix in their name are suitable for preparing membranes for fuel cells or electrolyzers. Since these products are based on a chemically-stabilized polymer, they will exhibit superior durability in systems that involve radical species such as •OH, •OOH (hydroxyl and hydroperoxyl radicals) and the like.

It is not feasible to prepare cast films directly from water-based Aquivion® PFSA dispersion concentrates (products containing a B suffix) because a coatable formulation also requires organic solvents such as certain alcohols, pyrrolidones, dimethylsulfone, DMSO, or other common solvents with suitable physical properties.

Organic solvents are also used when starting from Aquivion® PFSA powder grades (products containing a PW prefix), which are dispersed directly into a solvent or mixture prior to the casting process.

Figure 1: Close-up of membrane production

It is feasible to prepare a thin (< 50 microns) cast film using Aquivion® D83-06A as this ready-to-use dispersion is already formulated with alcohols and has a polymer concentration of 6 % by weight. As a prerequisite, the typical rheological behavior of D83-06A must be compatible with the coating equipment being used.

When the resulting solid content of a formulation made from Aquivion® PFSA dispersion and solvents is inferior to the desired value, one can first increase the polymer concentration of the Aquivion® PFSA aqueous dispersion from 24-25 % w/w up to a maximum of 35 % w/w by heating the liquid to no more than 60 °C (140 °F) while stirring. The concentrate will have a shorter shelf life; however, it can be used in formulation procedures as described hereafter and result in a coating formulation with a higher final solid content.

Formulation Development

Formulators optimize the following primary parameters when adjusting coating line formulations:

- Rheological behavior
- Surface tension and consequent wetting behavior
- Film forming properties at target film thickness
- Desired solid content

After adding the organic solvents, the viscosity of the formulation will change immediately and may continue to increase slowly as a function of time, temperature, solvent type and polymer concentration. For this reason, producers prefer to prepare coating formulation batches just prior to using them in a coating run. To limit viscosity changes over time, store the formulated dispersion at a low temperature, e.g., in a refrigerator at about 5 °C (40 °F).

To achieve a higher viscosity formulation, increase the PFSA polymer content and/or the solvent-to-water ratio. For example, a higher percentage of isopropyl alcohol (IPA) will quickly and significantly increase the viscosity of the formulation. Be aware that the PFSA polymer matrix can easily form a gelled, swollen, solvated mass that cannot be coated. The same will occur to a more moderate extent when using 1-propanol instead of IPA.

Typically, a higher PFSA solid content is expected to require a reduced content of polymer-swelling organic solvents. This keeps the resulting formulation's viscosity level within reasonable limits that are suitable for the following film-coating step.

Coating

The schematic shown in Figure 2 includes a common sequence of coating and subsequent solvent removal steps used to form a cast membrane and to improve its mechanical properties as the solid structure consolidates.

1. Start with a temperature (T1) that is slightly below the most volatile solvent's boiling point to evaporate low boiling solvents rapidly while preventing the creation of bubbles.
2. Increase the temperature (T2>T1) to complete the removal of all volatile solvents, including residual fractions that have a higher evaporation temperature.
3. Raise the temperature (T3>T2) to 190-210 °C (374-410 °F) to improve the durability of the obtained film. A minimum of 12 minutes around 190 °C (374 °F) and 6 minutes at about 210 °C (410 °F) is a suggested starting point for a production fine-tuning.

This procedure will need to be optimized for specific equipment and product requirements. In any case, the glass-transition temperature (T_g) of Aquivion® PFSA is in the range of 120-140 °C (250-285 °F) and the polymer is thermally stable up to 230 °C (445 °F).

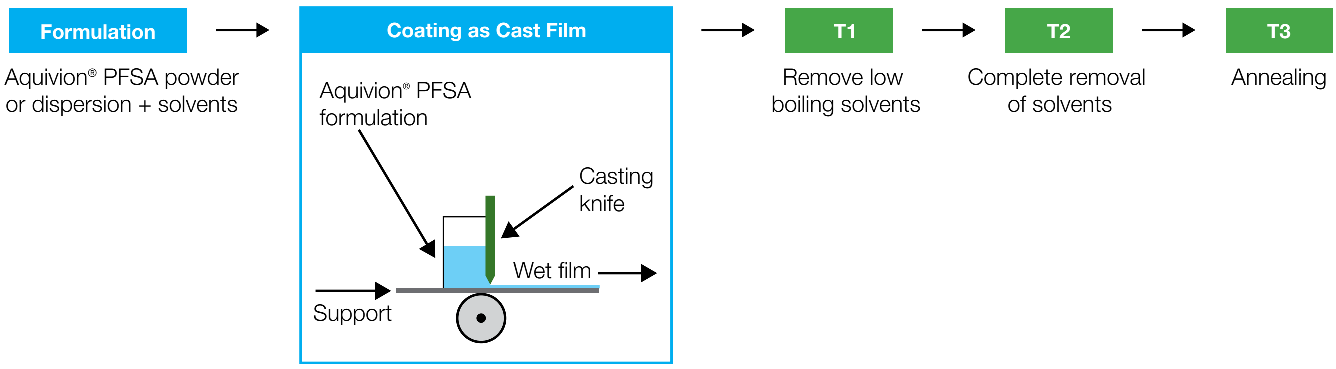
Should the membrane darken during the thermal treatment at T3, the following may be root causes of the discoloration:

- Incomplete removal of solvents (especially when thicker membranes are produced)
- Insufficient oven ventilation (i.e., saturation of gas phase with solvent vapor)

First operational use of membranes may reveal a conditioning period during which trace residues of production solvents still leave the membrane. This particularly applies to electrochemical applications like PEM fuel cells or electrolyzers which operate in the absence of liquid acid. When a shortened membrane conditioning period is of interest, the following options exist:

- Select either more volatile solvents or solvents with lower chemical interaction with the PFSA's functional groups
- Refine production parameters for solvent removal or annealing
- After annealing, and prior to using the membrane in the application, apply a washing step with acid

Figure 2: Schematic for preparing a cast membrane



Solvent decomposition can be catalyzed by the strongly acidic SO_3H moieties of Aquivion® PFSA. It should be noted that in virtually all cases, such membrane discoloration will not lead to a reduction in the part's electrochemical performance. If desired for aesthetics, many such discolorations can be removed through a membrane post-treatment in diluted hydrogen peroxide and/or acids.

Web Impregnation

The procedure illustrated in Figure 2, including the same solvent removal steps, can be used to produce a reinforced membrane, but in this case the coating step is a web impregnation process.

Production of reinforced PFSA ionomer films is fundamentally a straightforward and standard process for everyone skilled in the art. Reinforcement structures can be either woven or non-woven fabrics with wide open spaces or even microporous structures. First, the web should be fully imbibed to result in a complete filling of its entire void fraction by PFSA ionomer. To achieve this, some considerations require general attention:

- The particle size distribution of PFSA in the impregnation formulation needs to be compatible with the pore size distribution of the web that one intends to fill
- The final formulation shall be able to wet both the outer and inner surfaces of the web structure (adequate surface tension is needed)
- Solid PFSA content in the formation needs to be high enough to achieve a complete filling of all open spaces inside the web in the course of a single or multiple impregnation steps

Several seconds of contact time may be required for the colloidal PFSA nanoparticles to enter inside the web's porous structure, especially when a sub-micron porosity would need to be filled.

If further assistance is needed, please contact a Solvay service representative for support. For further characterization data, visit **www.aquivion.com**.

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