



## PURIFICATION OF METALS FROM ORGANIC SOLVENTS

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### Purpose

This application note introduces Protego® Plus LTX as an effective way to purify metal ions from organic solvents.

### Background

As semiconductor manufacturing processes continue to migrate to smaller technology nodes, there is an increasing need for greater control of particle and metallic contamination on wafers. Control of particulates in liquid fluids has been investigated for many years by using filters for removal of fine particles. With the latest technology nodes, filters rated for removing particles sub-20 nm in size is becoming standard practice during cleaning and etching chemical processes.

The control of metallic ions in fluids has been considered as a critical way to improve device yields during wet cleaning processes. Entegris introduced the Protego series of metal ion purifier + filter products to address the metallic contamination that may be found in DI water that is used in critical rinse and dilution applications. Protego products have been proven to improve process yield due to improvements in Minority Carrier Lifetime performance.<sup>1</sup>

In recent years, the metallic cleanliness of organic solvents has also been found to be a critical issue for wafer processing and enabling yield. This desire for high-purity chemicals is leading chemical and IC manufacturers to research ways to further reduce contamination in critical solvents. IC manufacturers need wafer protection solutions at the point-of-use (POU), while industrial chemical manufacturers need the ability to filter and purify in bulk. Typically, chemical manufacturers have utilized distillation methods for chemical purification, but the environmental and economical issues of distillation need to be taken into consideration.

Purification of metals and metal ions from organic solvents is not straightforward because the behavior and chemical form of metals vary with solvents and metal species. A significant amount of research and analysis needs to be done to understand the purification of metals from solvents. This paper introduces Entegris' Protego Plus LTX liquid purifiers as a solution to the needs of many users. A review of the challenges faced in solvent purification is also covered, along with experimental results for removal metals from PGME (propylene glycol monomethyl ether) and MeOH (methyl alcohol).

### Experimental Results

#### Protego Plus Purifier

The forms of ion-exchange adsorbent media are generally classified into two categories: beads and membranes. The structures of each make a difference in the removal efficiency of ion-exchange media. The adsorption mechanism of the beads is that the adsorbates diffuse into micropores in which many ion-exchange groups exist on the internal surface. In this beaded media, the removal efficiency is dependent upon the flow rate. Resin



Figure 1. Protego Plus LT/LTX metal purifier products.

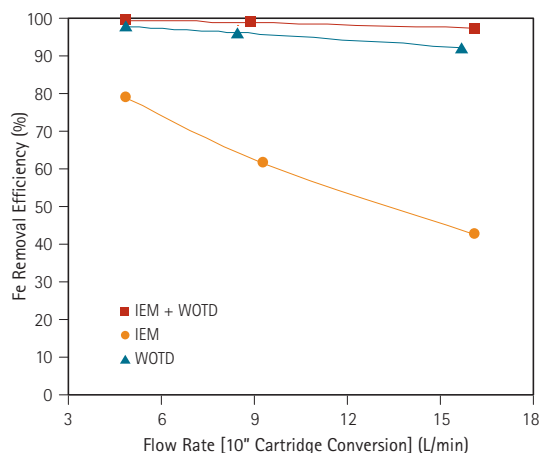


Figure 2. Iron removal efficiency from IPA solvent as a function of flow rate using Protego Plus LT (concentration of iron: 170 ppb; sample: 47 mm disk).

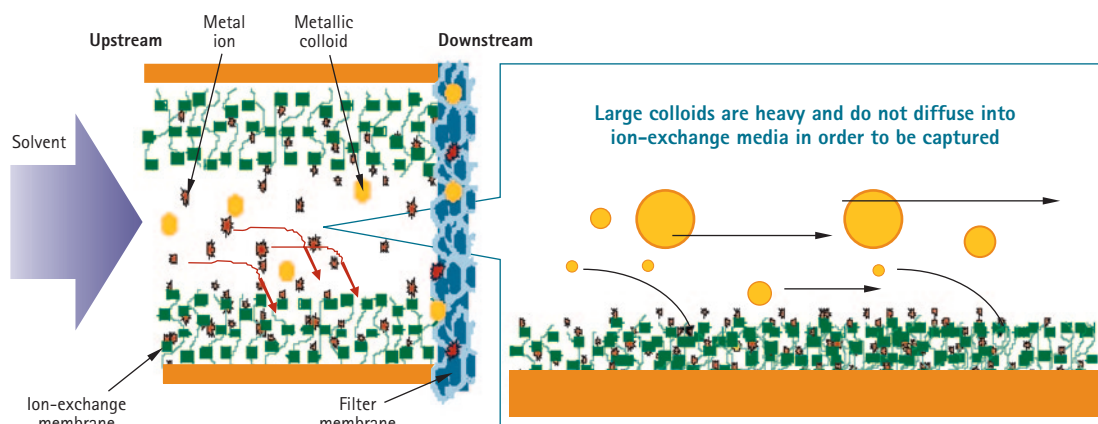


Figure 3. Removal metals in an organic solvent by ion-exchange and filter membranes.

swelling of the ion-exchange media is possible in organic solvents that cause the flow to be reduced and less efficient removal of metals. Ion-exchange membranes are based on functionalized, nonwoven fabric manufactured by graft polymerization. The membrane type has higher density of ion-exchange groups on the surface of the media, which allows the ion exchange to function effectively, regardless of flow rate and solvents.

However, it is not satisfactory just to purify metals with only ion-exchange membranes. Figure 2 shows the experimental results for removal of iron from IPA (isopropyl alcohol). This result suggests that it is better to fabricate metal purifiers with both ion-exchange and filter membranes.

In chemical solutions, especially organic solvents, multivalent metals like iron have a tendency to form charged colloids, which have broad mass distribution. The ion-exchange membranes efficiently capture metal ions and small colloids due to electrostatic interaction. However, the large colloid particles are too heavy and cannot diffuse into the ion-exchange functional groups against liquid stream; thus colloid particles cannot be removed easily, as shown in Figure 3. For these colloids, filter membranes are capable to capture and remove them from the fluid stream.

Taking this into consideration, Protego Plus LT and LTX products (Figure 1) are designed to have both purifier and filter membranes to aid in the removal of particles containing metals and metal ion forms.

**Properties of Organic Solvents Impact Removal Metals**

The removal of sodium and potassium metal ions from both PMGE and an aqueous solution using Protego Plus ion exchange is shown in Figure 4. Protego Plus efficiently removes sodium and potassium from an aqueous solution even at different flow rates. In PGME solvent, potassium is effectively removed. However the removal of sodium in PGME solvent is reduced as the flow rate increases. This indicates that in PGME solvent, metals exist not only as dissociated metal ions but also as metal salts. This must be taken into consideration when purification of metals from organic solvents is implemented.

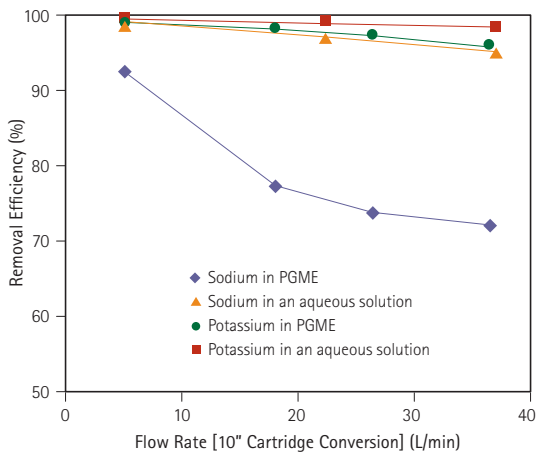


Figure 4. Flow rate and removal efficiency of sodium and potassium in both PGME and an aqueous solution using Protego Plus LT (Aqueous solution: concentration Na 15 ppb, K 34 ppb; PGME: concentration Na 15 ppb, K 37 ppb; Sample: 2 x 25 mm Protego Plus ion-exchange membrane media).

It is known that in high-relative permittivity solutions like water, metal salts and ion-exchange groups are completely dissociated into ionic form. As the permittivity of the solution decreases, metal salts are less likely to dissociate into their ionic species.<sup>2-5</sup> The permittivity of PGME is much lower than that of water; so it is believed that the sodium removal efficiency in PGME would be suppressed by the reduction of ionic species.

The result of the ion-exchange membranes dipped in both PGME and an aqueous solution also suggests that the adsorption behavior of metals

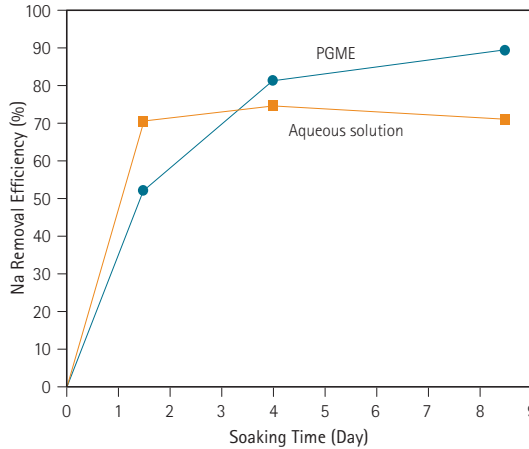


Figure 5. Adsorption equilibrium on sodium in PGME and an aqueous solution (Molar number of sodium corresponds to about half that of ion-exchange).

depends on the properties of organic solvents (Figure 5). Considering the time for reaching the adsorption equilibrium, the one in PGME is much longer than the other because of a lower dissociation degree of ion-exchange groups and metal salts. In other words, metal salts have a stronger binding affinity in PGME than in an aqueous solution. This is true for ion-exchange groups as well.

**Purification of Metals From PGME and MeOH**

The experimental results of metals removal from PGME by recirculation filtration is shown in Figure 5. This test was performed on a small scale under conditions that will represent the real situation for a storage tank in a manufacturing plant.

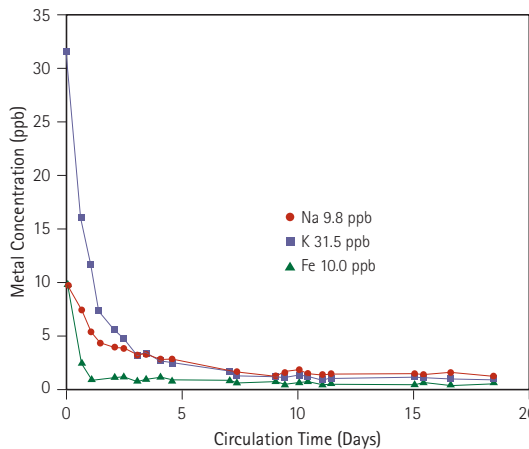


Figure 6. Purification of metals from PGME by Protego Plus using recirculation bath.

The actual size of a tank in a plant can contain 300,000 liters of PGME. The PGME was recirculated through nine 30-inch Protego Plus LT 0.05  $\mu\text{m}$  metal purifiers at 60 L/min in parallel. The PGME used in this test is from a commercial chemical manufacturer and its metal concentration is relatively high because of contamination through transportation.

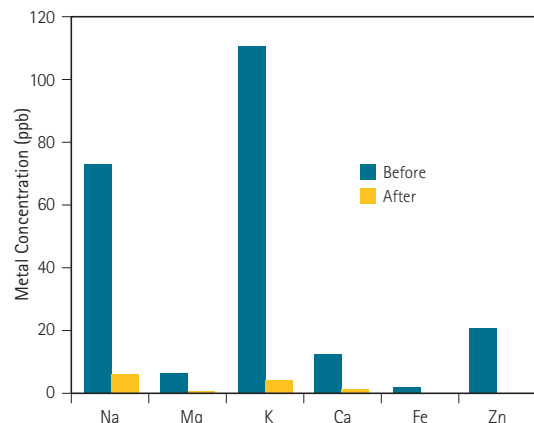


Figure 7. Purification of metals from MeOH by single-pass filtration using Protego Plus.

Sodium, potassium and iron were reduced down to a concentration of less than 1 ppb (removal efficiency >88%) after a week of recirculation. The total amount of metals removed corresponds to about 24% of the total ion-exchange capacity of six Protego Plus purifiers.

The results of purification of metals in industrial grade MeOH by single-pass filtration is shown in Figure 7. A chemical manufacturer improved the quality of the MeOH by using a Protego Plus LTX liquid purifier for metal purification and particle filtration. In this case, the concentration of alkali metals is high compared with other metals. Alkali metals are abundant in the environment and they have a greater chance to get into the chemicals during manufacturing process. The results show that the Protego Plus purifier can effectively remove even high levels of alkali metals, which are typically difficult to remove because alkali metals have low affinity to ion-exchange functional groups, among other metals.

## Discussion

As shown in the experimental results section, the Protego Plus LTX liquid purifier can efficiently remove metals from various organic solvents and can be used in a wide range of applications. For example, Protego Plus can be used in POU spray applications containing trace metals as well as in bulk purification. Protego Plus is currently being used effectively for purification of alcohols, PGMEA (propylene glycol monomethyl ether acetate), ethyl acetate,  $\gamma$ -butyrolactone and n-octane etc.

When implementing purification, one should be aware that Protego Plus can decrease the purity of some solvents. The strong acid ion-exchange function groups in the Protego Plus media can trigger hydrolysis or condensation reactions to esters or ketones. Moreover, Protego Plus purifiers will leach out some organic impurities, especially in aromatic hydrocarbon solvents. Nevertheless, considering the environmental and economical issues of solvent distillation, the removal of metals using ion-exchange purifier and filter products can be a promising approach to purification with some solvents.

## Reference

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