

UPW TREATMENT AND SYSTEM WITH ORGANIC NITROGEN REMOVAL

BACKGROUND OF THE INVENTION

This invention relates to water treatment in volume for high purity water applications where the product water is required to be free of trace contaminants. A particular embodiment relates to water treatment for semiconductor processing. For purposes of this invention, "high-purity water" refers to waters including so-called deionized water, ultrapure water and also to ultrahigh purity water; that is, to water produced, typically for industrial applications, by removing suspended solids, ions and non-ionic substances to a high or substantially complete extent, as judged by applicable assays. The invention is of particular utility in producing water that is to be free of trace contaminants, such as urea and organic nitrogen contaminants, and to contaminants that, for one reason or another, may be present at extremely low levels, or mask or otherwise escape removal or detection. The contaminants may be chronic, or may appear erratically, and they may be detectable or undetectable by standard analytical or in-plant instrumentation.

By way of example, such contaminant-free product water is required for semiconductor processing applications, where a fabrication plant may employ the treated product water as process or make-up water on a continuous basis at the rate of hundreds of gallons per minute to make up or to replenish various cleaning, developing, rinsing, etching, humidification and other process fluids employed in their fabrication processes.

The input feed stream for such an application may come directly from a natural source, such as a lake, river or well, but more typically comes from an already-treated supply, such as a municipal water supply, in which a certain degree of pretreatment may have removed a portion of solids, organics, hardness materials and/or ionic burden to bring the pretreated water into compliance with drinking water standards.

Even when such municipal water is the input (or "feed") stream for a high purity water treatment process, typically, the treatment of the input stream must address a range of impurities

present in the feed stream that, while acceptable or even desirable in the local water supply, would cause problems in the intended application. For example, a higher degree of filtration is necessary, as well as removal of metals commonly found in local water supplies that would impair semiconductor processing steps or increase the level of chip defects in finished wafers that have been exposed to the water. The municipal water treatment already undergone by the feed stream may also have introduced certain materials, such as softening byproducts, disinfection materials or byproducts, biocidal residues, conditioners or other matter that must be specifically addressed by the fabrication plant water treatment system to assure acceptable quality. The water supply may also present a level of organic contamination from mold and algae that colonize the reservoirs, valves and conduits of the supply.

Over the course of many years, particular problem contaminants have been identified, and appropriate treatments have been developed to address those contaminants that are present, or are likely to be present, at each plant. Local operating procedures may also have been developed, for example, to synchronize use of the municipal water with periods when the local feed water can be treated effectively (e.g., avoiding usage for a short period following a municipal plant cleaning operation when chemical injection is high or circulating algae could foul fab plant water treatment membranes or resin beds.)

By way of overview, a high purity water treatment plant or process may be viewed as generally requiring a pretreatment unit for removing suspended solids contained in raw water, a non-ionic substance removing unit for removing non-ionic substances from pretreated water, and an ion removal unit for removing ions from the water. Portions of these units or stages may be subsumed under the operation of the municipal water supply that at least partially pretreats the feed stream. Thus, typically municipal treatment removes a major portion of suspended solids, and may reduce or change the ionic load when coagulation and microfiltration, or reverse osmosis, treatments are applied. Municipal treatment may soften water, add coagulants and remove scale-forming metals when these are present at high levels, and typically will remove a substantial portion of toxic heavy metals if these are originally present.

Once such a municipal supply is received by a semiconductor water plant, the in-plant treatment of the resulting feed stream, in addition to achieving a higher degree of purity by further filtration, deionization, demineralization and degasification of the water, typically must address the biological growth that occurs in supply system conduits and tanks. High levels of deionization are typically achieved by distillation and/or flowing the water through units such as reverse osmosis, electrodialysis or electrodeionization devices and/or ion exchange beds. Organic compounds may be introduced or reintroduced by organisms that colonize conduits and tanks in the system, and often these are addressed by one or more steps such as microfiltration, capture in activated carbon or other beds, or by breakdown with ultraviolet radiation or ozone in addition to the above-listed ion and small-molecule removal processes.

An in-plant high purity water system may present design problems of various types. The plant must initially be designed to address the range of anticipated feed waters and achieve a constant minimal level of water quality. Beyond the factors of capital cost and operating expenses, and the environmental considerations raised by the volume of waste water produced as a by-product of the contaminant-removal treatment processes, various unanticipated problems may arise. The periodically-performed process of regenerating an ion exchange bed, or the unanticipated fouling of a membrane-based treatment system (an RO, ED or EDI unit) in the treatment line, may destabilize the treatment process or unexpectedly impair the quality of the output stream. One seeks to detect problems of this type by the use of monitoring instruments, such as a conductance meter or total organic carbon (TOC) monitor on the output stream. Even so, the continual introduction of new fabrication technologies requires plant operators to frequently ascertain whether existing water quality specs and operating procedures remain sufficient.

Because the normal output water of a high purity treatment plant has such low levels of contaminants, the appearance of an unusual trace contaminant may go undetected when the overall level of the class of contaminants, such as TOC, appears to remain within generally accepted levels. In that event, observation of variation in a process parameter (such as the stability of an exposure/development process) or a decrease in quality of a manufactured product (observed, for example, as an increase in number of defects in a semiconductor wafer) may

provide the first indication that the product water has experienced a detrimental change. In this case, investigation is needed to identify the responsible contaminant or treatment unit, and to develop procedures that will, in the future, prevent such quality deviations or detect the responsible agent before it affects the production line. Production down time is quite costly, and the observation of unexplained defects or process variations raises the possibility of additional undetected latent defects, and thus evokes the prospect of defective manufactured products further down the manufacturing train.

By way of example, it has been found that the presence of boron in the product water of a semiconductor fab plant may impair a number of semiconductor processes unless its presence is specifically addressed (for example by a special boron removal unit.) Some fab plants have therefore adopted a conservative approach, removing boron to a very low level, for example by a boron-selective resin column or bed, as shown, for example, in U.S. Patent No. 5,833,846. More recently, it has also been observed that with a suitable detector, the presence of boron in the treated product stream may be used as an early indication of impending exhaustion of an ion exchange resin and thus provide a warning before destructive breakthrough of other ions. The development of a sensitive boron monitor by one instrument maker, Sievers Instruments, Inc., as described in the published International Patent Application WO 02/12129, has now allowed this detection to serve as an indicator to allow efficient maintenance operations to replace ion exchange beds and prevent costly shut-down of manufacturing production. This allows detection of a threshold boron level to be used as a control step, e.g., to schedule bed replacement or regeneration before occurrence of leakage of other more destructive ions through the treatment plant into the product output stream or past the final polish.

For various other applications in electronics fabrication, pharmaceutical, chemical research, medical, food or even drinking water industries, other trace materials may be significant, yet their presence at trace levels poses an obstacle to their real time detection or recognition, and to their timely removal. In the area of microelectronics, as semiconductor fabrication plants evolve toward lithography with feature size at or below 0.1 micrometers, the presence of various organic or other molecules and materials in the product water may become increasingly more critical. See, for example, *Identification of a Critical UPW Contaminant by*

Applying an Understanding of Different TOC Measuring Technologies, Rydzewski, J., 2001 Watertech Conference (Dec. 4, 2001, Portland Oregon).

It would therefore be desirable to provide a treatment method, material or apparatus that directly treats the presence of a trace contaminant in a treatment stream of a water purification plant such that the contaminant is removed and is not present in the product water stream.

It would also be desirable to provide such a treatment method, material or apparatus that resides in the product line and operates effectively without requiring a measurement, detection or specific control action for its operation.

It would also be desirable to provide such a treatment method, material or apparatus operating in response to a process measurement or detection, to address the contaminant while minimizing introduction of other trace contaminants to a level within the removal capacity of the other treatment units of the system.

It would further be desirable to provide a removal system that resides in the treatment line such that it may be activated seasonally, or on-demand, as required without meanwhile impairing or complicating other treatment processes.

SUMMARY OF THE INVENTION

One or more of the foregoing desirable ends and other favorable results are achieved in a high purity water treatment system wherein a feed fluid possessing a trace amount of a possibly undetected, non-ionic or otherwise non-removed contaminant is contacted in the flow to trap and/or convert the contaminant, and the contaminant or conversion products are removed from the flow, reducing the contaminant level.

The present invention involves treating a large amount of plain water, illustratively to selectively remove an organic nitrogen contaminant that is present in trace amounts. By plain water is meant water that has either been, or is being, treated to make pure product water. This may be distinguished, for example, from water in the form of a one-, or multiple-phase chemical

solution, an aqueous slurry, or other water-based manufacturing process fluid. By organic nitrogen contaminant, is meant a relatively small dissolved organic nitrogen-containing molecule, and typically a contaminant that is only partially removed by filtration or ion-removal units, or that appears in a treatment system or at a stage where appropriate removal capability is not present.

In its broad aspects, the invention contacts the water with either a controlled amount of an active agent, or an immobilized active agent, that is effective to selectively reduce the amount of contaminant, which may be present at only a trace level, to a significantly lower, and thus acceptable, level. This reduction may be accomplished by conversion to removable sub-units, by direct capture, or a by combination of capture and at least partial conversion to removable form.

Preferably the flow is contacted to an enzyme or to an active bound material that cleaves or otherwise breaks down the contaminant (e.g., into one or more ionizable or otherwise removable units such as gases or other molecules). The ions or breakdown products are removed (e.g., by one or more treatment units that remove the ions and gases or other molecules), producing a high purity product flow that is essentially free of the trace contaminant. The trace contaminant may be a contaminant that is highly undesirable in a particular manufacturing process context, such as urea or other nitrogenous organic species present in the TOC component of a semiconductor product water. (Urea, for example, has been found to pass through a UPW treatment line and to impair self-catalyzed or acid-catalyzed lithography processes at trace concentrations.) In one aspect, the feed water may be contacted to an affinity trap to remove, or may be contacted to an enzyme, such as urease, to effect ionization or breakdown of, the trace contaminant.

In one embodiment, an enzyme, such as a lyophilized urease solution, may be injected into the treatment stream to specifically promote or catalyze removal of the contaminant present in the bulk flow of water. A detector responsive to trace levels of the target contaminant may provide a feedback signal to control injection of the enzyme, and a reaction tank may be provided to assure suitable overall delay for adequate contact time of the contaminant/enzyme system. A recirculating flow loop may scavenge and recirculate enzyme, allowing high

concentrations of the enzyme to be economically applied and operate with a shortened reaction time.

In other embodiments, an enzyme or other active agent may be immobilized on a support. The support may comprise beads forming a bed or column, or held in a cartridge, through which the feed flows to provide intimate contact. This assures that the contaminant, even when present at low concentration or at a level that is not detectable by typical water treatment instrumentation in the feed stream, will encounter and be cleaved by the enzyme or agent. In another embodiment, the support may be a membrane, such as the semi-permeable membrane of a reverse osmosis (RO), microfiltration (MF), ultrafiltration (UF) or nanofiltration (NF) unit. The membrane may be the membrane of a cross flow or other filtration module, such as a spiral wound or a hollow fiber module. The membrane and module may otherwise be of conventional type, and the enzyme or agent may be immobilized onto the membrane in a post-fabrication treatment process. The membrane or module may also be a dead-ended type of unit. A suitable membrane unit may be obtained by activating the membrane present in a commercially available cross flow filtration cartridge or module. For example, the membrane may be surface-activated by passage of a dilute solution of the appropriate enzyme through the unit such that enzyme is captured in or on the membrane of the module. Preparation of the membrane to initially bind or to better retain the enzyme, may be enhanced by a preliminary step of membrane cleaning or another treatment, e.g., for surface activation. Retention or binding may also be enhanced, e.g., by following the enzyme treatment with glutaraldehyde once the enzyme is in place and/or by a cross-linking step. Uniformity and extent of binding of enzyme to the membrane may be enhanced by circulating the enzyme in a low-concentration solution or carrier through the module in a flow loop for an extended time, minutes or hours, to achieve a more uniform distribution and greater surface concentration of bound matter. A specific example of the foregoing embodiments may employ urease as the enzyme or active agent to reduce the level of contaminant urea.

The enzymatically-treated membrane unit is then operated in its normal sense, e.g., as a reverse osmosis or microfiltration unit at an appropriate stage of the water treatment line. In operation, the pore structure of the membrane provides a large effective area at which the feed

fluid is brought into close proximity or intimate contact with the surface-bound enzyme, so that even though the trace contaminant is present at low concentration, the relative rate of contact or capture of the contaminant is high, and the immobilized enzyme effectively reduces the already-low level of trace contaminant.

In other embodiments, the active agent or enzyme may be immobilized on beads or microparticles that are themselves movable and may be injected into the flow stream, or into a mixing or reaction tank in the flow path. The treatment line may be configured such that the bead or microparticle substrate passes through various treatment units where fluid may be processed, filtered or degasified, and the substrate is recovered, regenerated, or replenished and recirculated.

The targeting of low levels of impurity in a large-volume or high-flow bulk treatment of water presents highly unfavorable rate limitations on removal. By immobilizing the active agent on a high surface area substrate – on a porous membrane or on particles of small diameter, systems of the invention are to achieve effective removal or destruction rates despite the low concentration and generally unfavorable reaction dynamics of the targeted contaminant. In particular, a micro- or macro- porous membrane may operate to bring the product being treated into close proximity (within the pore diameter) to the surface-held agent, while the membrane or even a rough-surfaced thin film, or a microparticle infusion, will present a greatly enlarged surface area. Effectiveness may be further enhanced by choice of appropriate reaction dynamics: by using an enzyme or removal reagent that catalyzes hydrolysis, the reaction rate will not be dependent on additional cofactors or the like which would typically be present only at low concentration or even be absent from a treated flow.

In general an enzyme or other active process may produce breakdown products that are ionic or ionizable, or include gases or small molecules. These are then removed from the feed stream, by a suitable treatment unit, which may be the same or a different membrane or other treatment unit. Preferably, one or more downstream units may effect the removal of the breakdown products from the treatment stream. For example ammonia and carbon dioxide produced by enzymatic cleavage of urea may be removed by electrodialysis (including EDI), by

ion exchange resin beds, may be addressed by an RO unit, or may be removed by a downstream degasifier. When dealing with ultrahigh purity streams, an enzymatic cleaning unit, contact loop, reaction tank or bead- or membrane-bound treatment unit may be placed in an upstream position of the line to assure that any material that it might shed will itself be removed and will not reduce quality of the final product water.

Systems of the invention may also be implemented with non-enzymatic active agents. In addition to various agents specifically discussed hereinbelow, these may include catalysts of all types, both organic and inorganic. The active agent may capture the trace contaminant, or may capture and react with the contaminant to release a smaller group or sub-unit. In general, the capture embodiments of the invention may be placed further downstream in the UPW treatment line. If a capture-type contaminant removal unit effects no release of sub-units, then the removal unit may be placed far downstream, e.g., in a polishing loop with the product water storage tank, as is sometimes done with chelating resin beds to effect the cleanup of trace contaminants. When the capture unit is enzymatic or else operates by covalent reaction and release of a moiety (e.g., of ammonia), then the unit may be positioned further upstream of one or more treatment units of the system that remove, or convert and remove, the released by-product.

In one embodiment, the trace contaminant may be removed by contacting the flow to a so-called affinity medium, such as the resins or membranes sold for chromatographic or biological separations, for example, by Pall Corporation. A suitable membrane or resin may, for example, have ketone, diketone, amine, hydrazine, hydrazide or aldehyde functional groups, and the contaminant is captured by covalent attachment to remove it from the treatment stream. The medium may take the form of a membrane, a particle bed or other substrate. See, for example, United States Patents No. 4,824,870, 4,961,852 and 4,992,172 for discussions of some suitable membrane chemistry. Since the contaminant is present at very low levels, the capture element may have a reasonable lifetime, and may be simply replaced when the affinity medium becomes exhausted. In other embodiments an affinity medium may be employed as the substrate to bind an enzyme or other targeted capture or reaction agent for removing the contaminant. In other embodiments, residual functional groups, such as amino- or carboxylic acid functional groups, such as those remaining from the interfacial polymerization reaction in a thin film composite

(TFC) membrane, may be used, optionally with suitable linkers if necessary, to attach the enzyme at the substrate surface while preserving its activity.

In embodiments intended for semiconductor UPW fab water production, where the level of urea (and of TOC generally) is to lie below a low limit, a recognized problem has been that use of the UPW product in a plant humidification system produces nitrogen-bearing particulate contamination when urea persists in the product water. This problem is addressed in accordance with another aspect of the invention by providing product water to a non-spray-type humidifier, for example a humidifier operating by evaporation from a wetted web, such that aerosols and particles are not formed, or such that the urea/organic contaminant does not enter the humidified air. Urea may then be permitted at higher levels in the product, without introducing concentrated urea particulates. In accordance with another aspect, front-end treatment of the feed stream is optimized to limit passage of urea to the later stages. This may be effected by initial treatment with one or more RO stages or passes, wherein the RO membranes are selected for high urea rejection, so that any spike in level present in the feed is strongly attenuated after early stage treatment. In some instances where the urea rejection characteristics of a membrane are not known, its boron rejection may be used as a surrogate measure during membrane selection. Temperature, pressure or pH may be set to preferentially enhance this rejection characteristic.

BRIEF DESCRIPTION OF THE DRAWINGS

These and other features of the invention will be understood from the description and claims herein, taken together with the drawings illustrating details and representative embodiments of the invention, wherein

FIG. 1 is a schematic depiction of one embodiment of a high-purity water producing apparatus according to the invention and comprising an enzymatic treatment unit for conversion of a trace contaminant present in the feed flow;

FIG. 2 shows one representative configuration of a high-purity water producing system according to the invention;

FIG. 3 shows another configuration of a high-purity water producing system according to the invention;

FIG. 4 shows another configuration of a high-purity water producing system according to the invention;

FIG. 5 shows another embodiment of a contaminant treatment unit of the invention, usable in a high purity water treatment plant; and

FIG. 5A shows an embodiment similar to the system of FIG. 5 and configured to minimize shear damage of treatment material.

DETAILED DESCRIPTION

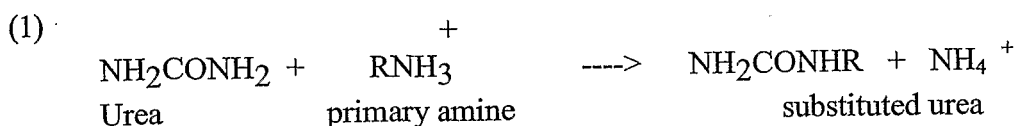
As shown schematically in Figure 1 a UPW treatment system of the present invention includes one or more units arranged as a UPW water treatment processing line 10a together with an organic nitrogen trace contaminant removal unit 10b that reduces the level of one or more organic nitrogen contaminants that may be present in the water. Typically the feed water input to the system includes a pretreatment unit 1. Pretreatment 1 may include municipal treatment, and/or where applicable, may include locally-applied pretreatments such as sedimentation, agglomeration, activated carbon, multimedia filtration, ultrafiltration, microfiltration or other preliminary water treatment of the input stream.

The present invention has been motivated by the recent discovery that urea present in trace amounts in the feed water to a semiconductor UPW treatment plant was passing through the water treatment line in the UPW product stream and interfering with proper operation of wafer lithography and other manufacturing processes. The urea was not detected by plant TOC monitoring instruments, and was not effectively removed by existing plant processes. That particular situation may have been caused by locally-applied agricultural chemicals sporadically entering the surface runoff; however similar and possibly undetected treatment problems are likely to arise from seasonal biotic flourishes and water system biota, and/or hydrological variations, such as changes in surface and subsurface flow contributions to the feed stream. All these sources of contaminants are all addressed in accordance with the present invention by a treatment system or method of operation wherein possibly undetected or trace contaminants are removed from the flow of a water treatment system by contacting to an active agent. That is, the agent is effective to reduce an already-low level to an appreciably lower level in the treatment plant. In the illustrative example, the agent targets one or more organic nitrogen-containing contaminants.

In one embodiment this is done by contacting the stream to an enzyme that converts the trace contaminant into products treatable in the product water flow. The enzyme may be a free enzyme, for example placed directly in the flow or in a reaction tank, or may be a bound enzyme maintained on a support in a flow-through treatment device or portion of the treatment line. The conversion or breakdown products may be removed by existing or additional elements of the UPW treatment 10a. In another embodiment the stream is contacted to an activated surface that either directly binds to, or that engages and cleaves, the contaminant. The activated surface may be the surface of an affinity resin precursor substrate or membrane, or a resin or membrane on which an enzyme is immobilized, or a resin or membrane which otherwise carries functional groups capable of binding to, capturing or reacting with the targeted contaminant.

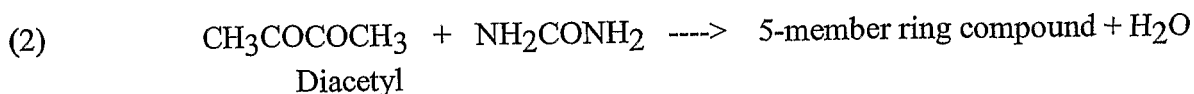
Thus, a membrane such as a microfiltration (MF), reverse osmosis (RO) or other membrane, a nickel-containing cation exchange membrane, or a depth filter or a resin bed, may have a coating, or have functional groups, adapted to specifically bind to and/or react with the contaminant -illustratively urea or other organic nitrogen compounds- present in the bulk feed water or the high purity product water stream.

One illustrative example is given by the reaction system (1)



This may be implemented with resin beads or membranes (microporous, UF or ion-exchange) having primary amine groups, preferably in salt form, to react with urea that comes in contact therewith, forming a substituted urea attached to the resin or membrane, and releasing ammonia as a by-product. The ammonia may be removed from the treatment stream by existing units of the system 10a. Another embodiment may be prepared by treating the membrane with a high molecular weight primary amine compound or polymer in solution, and building up a layer of this material against the membrane. The surface layer then reacts with urea present as a contaminant in the feed or product stream.

Another example is the reaction system (2)



Here, a diacetyl (or other dione molecule) is attached to resin beads or to a membrane support (such as a microporous, UF or ion-exchange membrane) and reacts with urea in the stream to form a five-membered ring captured on the support with water as the only by product. Other embodiments may add a high molecular weight dione molecule or polymer to the solution and build up a layer of it against a membrane or filter to react with the urea.

When preparing such a direct capture material, affinity membranes or precursor substrates such as those discussed elsewhere herein may be employed, as well as polymer-bound ketone, diketones, amine, hydrazine, hydrazide, and aldehydes. Copolymer and dip approaches may also be used. Adjacent CHO groups may form a coupling reaction to form MeOH at high aldehyde concentrations, and these are therefore to be avoided.

In accordance with another aspect of the invention, rather than a direct capture device in which contact with the contaminant binds a portion of the trace contaminant and breaks off a moiety for removal by degasification, deionization or the like, the contaminant removal agent may be directly injected into the flow of treatment water. For example, a urease solution may be added to the system feed water ahead of a reverse osmosis (RO) or other element of the UPW treatment line to specifically remove trace levels of urea contamination. Such direct addition of a contaminant-targeting treatment 20 is shown schematically in Figure 2. Preferably, the material, e.g., a urease solution, is added at a concentration effective to cleave the trace contaminant present in the water. As described further below in connection with Figure 5, urease addition may be carried out in a holding tank that provides the necessary residence time for complete reaction and removal to the low- or sub-ppb target level. The material so added may be either flushed, or advantageously recovered and recycled, as appropriate (depending largely on economics.) In this embodiment, the injected urease material acts directly in the flow. As further shown in Figure 2, the urease itself may be captured by a downstream element (UF 22) to

effectively remove it or recover it from the flow. For example, when urease is injected upstream of an RO unit, the large (approx. 255 by 65 Angstrom) elliptical biomolecule will be rejected by the membrane, and can be recovered by concentrating the reject stream with an ultrafiltration or nanofiltration unit as shown in Figure 2. Ions and the major part of the reject stream may be flushed to drain, applied to secondary purposes or passed to further processes, while the recovered urease passes to the inlet stream to maintain an effective enzyme concentration in the feed flow. Preferably, when injection of the enzyme or active agent is used, the injected flow passes through a mixing line and/or tank of a size effective to provide adequate contact time (e.g., in ppm-minutes) for reaction to occur. Injection of fresh enzyme may be controlled in response to a sensor on the permeate side of the system. Alternatively, rather than injecting upstream of an RO, the system may inject enzyme into the stream and simply remove the injected enzyme from the flow downstream by capture on a resin bed or membrane that binds to and immobilizes the enzyme, or by a UF or loose NF membrane that retains the enzyme but passes the rest of the fluid flow and smaller molecules. In the latter case, higher concentration levels of enzyme may be economically employed and/or greater effective contact time achieved, and the recovered enzyme remains active in the treatment line. Preferably such a downstream element is configured to be periodically backflushed or cleaned.

When injection of urease or other treatment described herein is to be controlled responsive to detected levels of contamination, detection may be effected using an instrument such as described in United States Provisional patent application (and it's progeny) Serial No. 60/336,871, filed by inventor Richard D. Godec on December 3, 2001, and entitled Sensitive Detection of Organic Nitrogen Compounds in Water. Such a detector may operate on the product side of a treatment plant, and may detect urea with specificity down to sub-ppb concentrations. That document is hereby incorporated herein by reference in its entirety. Detection may also be accomplished using a manual laboratory assay, with appropriate microquantitative techniques modified as appropriate for the urea measurand. For some embodiments, the treatment may be embodied in a side branch, such as circulation through a holding tank or passage through a membrane/filter unit, that is brought on-line only when the detection indicates a need to reduce urea levels.

In another embodiment of the invention, the trace contaminant is contacted to an immobilized agent selected to break down the contaminant without thereby depleting the agent. In a preferred embodiment, a suitable proteolytic enzyme is immobilized on a support, and the feed or product water stream is contacted to the support to cleave the contaminant. Thus, to address the above-mentioned urea contamination problem, a urease, an enzyme of about 480 kiloDalton size that catalyzes the hydrolysis of urea to ammonia and CO₂, may be immobilized on a flow treatment element to effectively treat water having trace urea (or other small organic nitrogen contaminant having a homologous portion or otherwise susceptible to breakdown by the urease). No oxidation or reduction occurs, thus no enzyme cofactors are required and the reaction proceeds at a high rate. The urease may be immobilized onto (e.g., impregnated into, for a porous or gel-like substrate) a treatment resin (e.g., ion exchange beads), a neutral support (such as biotinylated or otherwise treated glass beads) or other medium, such as a porous membrane or filter. Such immobilization is preferably performed with other material, such as a buffer material, that protects the urease functionality. Many technologies for immobilization may be adapted from techniques developed for medical, pharmaceutical, biotech or food industries in the attachment of trypsin, invertase, urease and other agents or proteases to supports in the context of synthetic, analytical or reactive processes. In the bulk water treatment processes of the present invention, it is desirable that the treatment system be effective to treat a large volume or high flow of water in which the contaminant is present at a very low level. The system utilizes one or more reaction-enhancement mechanisms that affect the reaction dynamics to achieve effective treatment, and these are discussed herein (e.g., catalysis, high surface-interaction area, a substrate pore structure to bring feed fluid and treatment material in contact, a recirculation loop or tank to increase residence/contact time.)

Figure 3 illustrates one such system 100, wherein a treatment water is passed through a semipermeable membrane, illustratively a dead-ended filtration (MF or UF) membrane element 30 having such enzyme deposited or permanently immobilized thereon or therein, as well as a number of otherwise conventional treatment elements (not separately identified) arranged in a UPW treatment line 10. The removal element 30 is illustrated as being upstream of the other elements of line 10, but in practice may be positioned one or more locations ahead, within or downstream of the other elements of the treatment line as described herein. For example, when a

UV treatment is provided to break down or oxidize TOC, the unit 30 may be positioned downstream of the UV so that it operates largely on organic nitrogen compounds that are substantially unaffected by UV, after a portion of the other TOC burden has been converted or removed. In a fab plant, the urea removal unit 30 may be positioned downstream of the entire primary make-up treatment process line, in a final polish with an ion exchange IX resin unit, or in a treatment loop with a storage tank that holds the product water (thereby advantageously removing contaminants due to systemic biota), rather than upstream in the primary make-up water treatment line. It will be understood that the unit 30 need not be an MF unit; enzyme (or reactive material as described above) may be immobilized on resin particles, in a temporary deposit on a membrane or depth filter, or on another functional membrane unit. While immobilization in a microfiltration membrane constitutes a currently preferred embodiment for immobilized treatment, systems may also retain the enzyme in a precoat (e.g., diatomaceous earth, a precipitant) that resides on a membrane surface. In this case, the precoat may be periodically backwashed to drain and refreshed. When an active agent or enzyme is effectively bonded to the internal pore surface of a microporous membrane, the pore structure assures that the trace urea, despite its low concentration, must pass within a very small distance of the surface (as determined by pore size), and this is expected to enhance capture/hydrolysis reaction dynamics. The membrane may be included in a flow-through module or cannister structure, either as a dead-ended or cross flow unit.

A number of existing membrane modules for UPW water treatment contain suitable substrates for immobilizing an enzyme or other active agent thereon, and other membranes not presently packaged in module form (i.e., not currently sold in a ported, spiral- or other cylindrical vessel package for direct plumbing into a UPW system) are readily adapted to such modules. Thus, when the membrane contains acrylamide units, it may be activated (e.g., with formaldehyde at 45 degrees Celsius and pH 7.5) and the agent or enzyme may be applied by a flow treatment through the module. This one-step reaction introducing N-hydroxymethyl groups may provide immobilization of an effective amount of the enzyme. Concentrations and reaction conditions may be varied to retain suitable microfiltration or other permeation properties of the underlying substrate while immobilizing an effective amount of the agent. The porosity of the membrane assures that substantially all of the treated water will be brought into close proximity to the surface-bound agent so that enzymatic or reactive breakdown will occur and the trace level

of contaminant will be effectively converted or removed. As noted above, other common classes of membranes and resins are readily employed as substrates.

Thus, for a macroporous membrane substrate, the enzyme may be bound by simple adsorption onto the surface. In other situations, covalent immobilization may be effected by treating the membrane so that it binds to the amino groups present in the enzyme. This may be done by introducing epoxy or aldehyde groups onto the membrane. For a material such as a polyamide thin film composite (TFC) RO membrane, it may be desirable to enhance the level of immobilization achieved by adsorption on the surface (which is relatively rough on a microscopic scale), by activating free amino groups (e.g., using glutaraldehyde) to provide a binding capability to immobilize the enzyme. Thus, good binding has been observed using Eupergit C (an epoxy-terminated polyacrylamide) and silica (as amino-derivatized CPG activated with glutaraldehyde). In some contexts, urease bound through Schiff's base linkages (via aldehyde-activated substrates) tends to retain its activity longer. See Chapter 4 of *Analytical Applications of Immobilized Enzyme Reactors*, S. Lam and G. Malkin, eds. New York: Chapman & Hall, 1994. Various other approaches may be used for binding urease. Thus one may make a thin film membrane with excess or unreacted acid chloride sites present, which are then reacted with the amino functionality of urease to bind the urease to the thin film. The unreacted amino or carboxylic acid functionality remaining in a thin film composite RO membrane after its formation by interfacial polymerization may be used to anchor a linking agent (such as glutaraldehyde to the amino groups) and covalently bond the urease to the aldehyde ending. Immobilization need not be on a membrane. One can, for example, react urease with benzyl chloride groups in a resin bead precursor material of anion exchange resin beads. Anion exchange beads are typically made by converting benzene rings in the styrene/divinylbenzene copolymer into benzyl chloride groups which are subsequently reacted with amines to form the exchange sites. This precursor resin could be urease-loaded and used in a resin bed or bottle located upstream of a mixed ion exchange bed or an EDI stack; the urease-loaded beads could also be placed as a portion of the beads in filled cells of an EDI stack, which in operation would then simultaneously decompose the trace urea present in the treatment stream and remove the decomposition products from the stream. When incorporating such beads into an EDI stack, the beads may be positioned in a discrete stripe or band in the EDI flow cells, or may be interspersed

with exchange resin beads. Various constructions (e.g., use of non-functional beads or of weak anion exchange beads, location at the front of the EDI dilute flow path, or suitable striping), may be used to protect the immobilized urease from localized pH extremes that might otherwise occur at regenerated bead and resin surfaces in an EDI unit.

Urease has been captured directly on anion exchange beads and has demonstrated high activity even after many months of use. Thus, commercially available resin beads may be used to immobilize the enzyme for use in EDI. The resins may be prefunctionalized before loading in the EDI stack, or may be prepared *in situ* by injecting the enzyme/agent in a flow entering the EDI stack. In the latter case, the resin may be reactivated by a similar process after each stack cleaning. Optimization of activity in an EDI cell may require additional precautionary steps, such as subpolarized operation or use of monotype or specific resins in the surrounding portion of the flow path, to maintain pH or other conditions that preserve or enhance activity of the enzyme. Applicant further contemplates using a weak base resin, an organic scavenging resin, or a non-charged resin, or to employ an ion exchange resin and poison the resin, either before or after urease is immobilized, to protect the captured agent from adverse pH conditions in use. By incorporating the resin so treated as at least a portion of the resin in cells of a polarized EDI apparatus, some biological protection is provided against organisms, protease and fouling, while the EDI apparatus itself then effects removal of the ammonia and CO₂ contaminant breakdown products from the feed stream. Various types of beads may be employed to hold the urease, including non-fouling resins (for example, macroreticular resins) and resins or substrates which are otherwise inactive or neutral (such as glass beads). Agar beads may be especially preferred for applications outside of EDI stacks.

As discussed above, the removal of contaminant may be effected by a specific enzyme, or by provision of reactive or catalytic functionality immobilized on a substrate. In addition to enzymes and the chemically-reactive functional groups discussed herein, applicant also contemplates activating a substrate with a synthetic enzyme functionality, for example, with a synthetic protein that includes a replica of the active region of a natural enzyme. As synthesis technology advances, these materials may offer increased activity, or more robust performance characteristics over a broader spectrum of pH or other conditions. However, since the invention

is primarily directed to treatment of large flows in an ultrapure water treatment plant, currently the more economical agents are expected to be natural enzymes or reactive functional groups as described above, which are presently available in quantity for industrial use from sources such as jackbean, pigeon pea, bacterial culture and other inexpensive natural materials.

In systems of the invention, when the enzyme or active agent is incorporated in an MF membrane, a relatively small number of membrane modules may be positioned, for example, ahead of the ion exchange bottles in a UPW plant polishing loop with the product water tank, thus economically removing trace urea present in a large UPW system. Alternatively, the contaminant removal units may be positioned upstream in a portion of the water treatment line. When used in a UPW line having a two-stage RO treatment, a preferred site for placement of immobilized reactant would be on the permeate side of the first RO stage. Rather than passing permeate through a specially-treated MF membrane, applicant also deems it useful to activate the back side of the RO membrane itself by suitable surface preparation and application of the active agent or enzyme to the RO permeate side. In performing such activation treatment, care must be taken to apply very low pressures that do not damage the module. Advantageously, in such position the activated removal surface – the backside of an RO membrane- is protected from biological fouling or digestion, and is not subjected to deleterious levels of cleaning agents or foulants. Once attached, a cross linking treatment, such as an *in situ* glutaraldehyde treatment, may be applied to enhance enzyme retention or treatment lifetime.

Enzyme may also be employed at the inlet to the treatment line, for example by injection at a flocculated sand filter so that it is captured at the filter and treats the entering stream. Similarly, the active agent may be incorporated in a cartridge filter, such as a fibrous packing, membrane or other cartridge-type filter unit ahead of the first stage pump or elsewhere in the system. The latter embodiments are particularly advantageous to address the contaminant problem in existing plants without requiring redesign and installation of additional capital equipment.

In embodiments of the invention wherein an enzyme solution is injected into the water stream upstream of a membrane unit or particle bed such that membrane or bed receives and

captures the enzyme, the system may then operate the downstream capture portion as described above for an immobilized enzyme. In this case, urease solution may be added intermittently, for example after a clean-in-place (CIP) operation or otherwise, to periodically re-activate the membrane or support, and maintain its level of activity for trace contaminant removal. Re-treatment with enzyme solution may also be effected in response to a downstream detector, which detects when the contaminant level exceeds removal capacity, or when the removal efficacy has dropped to or is approaching an unacceptable level. When the immobilized enzyme is subjected to a CIP operation, the cleaning steps may be modified or adapted so as to retain or prevent deterioration of the enzyme. For example, rather than an EDTA cleaning (which could remove or substitute the active nickel sites of a urease enzyme and thus diminish or destroy its enzymatic activity), a nickel-EDTA treatment may be employed. Applicant also expects that other Group VIII transition metals may be employed instead of nickel, and these metals may also be employed in other aspects of the invention to stabilize urease activity or revive activity of spent or damaged urease.

Various membranes or materials can be directly used for immobilizing enzyme to create a fixed element for trace contaminant removal. Thus, an UltraBind™ type of affinity membrane (product code: 66544 from Pall-Gelman science) typically used for specialized biotech purposes such as protein blotting, or Toyopearl™ type of affinity resin (or, e.g., periodate-activated agarose material such as Formyl-650M as listed in Supelco chromatography catalog), or a membrane with an aldehyde surface functionality, such as one containing an acrolein or other aldehyde monomer, may be used for this purpose. Rather than the enzyme, applicant also contemplates employing a stand-alone organometallic (macrocyclic) coordination compound containing nickel or other Group VIII transition metal ions on beads, membranes or fixed material in the flow, or as colloidal or complexed material in the fluid, to trap or decompose the organic nitrogen trace contaminant material present in the water being treated. Thus, such material may be added or fixed on beads or a membrane to operate as described above. Direct oxidation or breakdown with materials such as ozone or UV irradiation, by contrast are expected to be less effective than embodiments of the present invention because of the refractory nature of urea and other organic nitrogen contaminants, as well as the extremely low concentrations of contaminant available to absorb UV energy or engage in oxidation

reactions. With the present invention, use of enzymatic or covalent capture, immobilization of the active reaction or capture agent in the stream, and immobilization on a porous, semi-permeable or dispersed medium are each expected, independently or in combination, to greatly increase the effective rate and endpoint of contaminant removal. When the contaminant is both captured and at least partially broken down or cleaved, the removal of breakdown components from the bulk water stream may in some embodiments be effected by the existing treatment devices.

Figure 4 illustrates in a schematic way overall configuration of a UPW treatment plant such as used in a semiconductor fabrication application. The plant typically includes a pretreatment section 201 of suitable characteristics and capacity for pretreating the feed for the primary make up water, followed by a sequence of treatments 210. Commonly, a pressure pump feeds a reverse osmosis (RO) unit 215 and the water subsequently passes to an arrangement of one or more treatments 216 such as a second stage RO, ion exchange (IX), electrodialysis (EDI) or the like, followed by one or more UV, ion exchange or other elements in a polish stage. Treatment may include a roughing stage in which the water flows in sequence through cation exchange resin, anion exchange resin and a mixed resin bed. Additional operations of softening, degasifying, UV exposure, pH adjustment and the like may occur in or before one or more of the stages in the later treatment 216, or before RO 215, as appropriate. While not specifically illustrated, water from the treatment line 210 typically flows to a reservoir or tank, from which it flows through a final polish in a loop through the plant, being drawn off from the loop as needed in various locations to make the developers, wet etchants, conditioners, rinse, humidification and other process fluids required by plant fabrication processes. The loop returns to the tank. Typically UV and IX units in the loop maintain product purity, disinfecting, breaking down and removing systemic contaminants.

In the context of such a treatment plant, one suitable location for the removal apparatus of the present invention is a position at or downstream of RO unit 215. This may be done by enzyme injection into the feed stream at the inlet of the RO 215. It may also be accomplished by immobilizing the enzyme on the downstream side of the membrane of RO 215 (e.g., by an initial extremely low-pressure back-permeation operation that binds to the membrane without risking

delamination) or by injection at that position. Placement at this location protects the active agent from excessive exposure to foulants or cleaning agents (caustic, acid, EDTA etc.), while assuring that any shed products from biological or other degradation of the enzyme will be captured by the downstream treatment processes. When the treatment line includes a second stage RO, the removal unit of the present invention may alternatively be positioned as just described but at the second RO. Another useful approach, however, is to embody the contaminant removal agent in a treated MF module which is placed just downstream of the initial treatment stage(s), e.g., of RO unit 215. An MF cartridge advantageously allows a high through put to be achieved while requiring relatively small area of treated membrane (e.g., high flux).

The example has been described with respect to the removal of trace urea, a particular non-ionized and commonly unrecognized contaminant of surface waters that may appear in the feed water of a UPW plant and pass undetected in the product stream. This material has been found to have highly deleterious effects, for example on photo resist lithography processes exposed at short wavelengths that achieve high contrast via chemical amplification, such as acid-catalyzed development. The water treatment processes, materials and systems of the invention are more generally applicable to removal or reduction of trace contaminants that may be present in the total organic carbon "TOC", such as ureas, carbamates/urethanes, esters, amides and other material of systemic or external biological or environmental origin and other organic nitrogen material. For example, where potential contamination such as shedding from resin decomposition is not fully addressed by use of high temperature or otherwise more stable anion resins (such as the TSA 1200 resin and related materials sold by Mitsubishi Chemical Corporation), the present invention provides a valuable removal capability that allows a water plant to operate with reduced level of the trace contaminant in its product water.

By activating a microfiltration membrane with the active agent, high flows may be achieved while assuring a high level of surface contact effective to capture and remove the organic nitrogen or other targeted contaminant. Preliminary calculations indicate that activation of a small number (4-40) of standard eight-inch spiral wound or hollow fiber membrane modules can provide the capacity for effectively treating 600 GPM of ultrapure fab water contaminated with 10 ppb of urea.

Figure 5 illustrates details of a contaminant removal/water treatment unit 40 in accordance with another embodiment of the invention. Unit 40 operates on a stream of water 101a that is being treated, to produce a treated stream 101b from which the target contaminant has been substantially removed. The unit includes a holding tank or series of tanks or other hold-up volume in which the flow of water is exposed to the active (bound or free) contaminant-removal agent for a time effective to assure removal at the low concentrations of target impurity. The tank reduces hydraulic short circuiting, and is sized in accordance with the expected flow and the relevant concentrations and reaction rates of the system. The hold-up volume, which is illustratively shown as a single tank 110, receives the incoming stream 101a, and after a specified residence time, a treated output from the tank passes, via pressure pump 120, to a reverse osmosis unit 130, forming a treated permeate output stream 101b. The RO unit 130 may, for example be the first pass RO of an otherwise conventional UPW treatment plant, or in a two-pass plant, may be the second pass RO unit. The urease present in the pressurized feed is rejected by RO 130, and the reject passes to an ultrafiltration unit 140 which retains and recovers the active agent in the retentate 142, returning it to the tank 110. A detector 144 may be placed in the retentate return line, and injection of fresh urease into tank 110 (via an injection pump, not shown) may be controlled in response to the urease concentration detected by detector 144 so as to maintain a desired concentration or set point of urease. (As noted above, the set point may itself be determined, or the urea treatment loop itself switched on-line, in response to a detection of the urea level elsewhere in the system).

By operating in a closed loop with urease recovery in this fashion, unit 40 may maintain more economically a very high concentration (e.g., 100 ppm or more) of urease in the treatment tank 110 and in the short affected segment of the treatment line, enhancing the reaction time or the clearance endpoint. The urease employed in unit 40 may be free urease, such as a lyophilized jackbean urease solution, or may take the form of urease bound to a substrate, such as beads or microparticles, or encapsulated in microcapsules or a protective medium. In the latter cases, the recovery filter 140 may be a loose ultrafiltration or even microfiltration element rather than a finer filter element. The recovery loop may include an intermittent or continuous blow down and/or a particle filter or other device or configuration to control and remove build up of retained contaminants, enzyme degradation products, biogrowth and the like.

For attachment to particles, enzyme may be attached to microparticles similar to the MIEX DOC media, a water treatment bead that targets small dissolved organic carbon molecules, as sold by the firm Orica Watercare. Those beads are smaller than typical water treatment resin beads, and have a magnetic component that aids their separation in a tank, with a functionality that effectively captures smaller organic molecules. That resin normally finds use in effectively removing material that would otherwise form disinfection by-products such as trihalomethanes and the like in a typical drinking water system. When used as a support for urease or other enzyme, these or finer beads may constitute an effective immobilization support, while facilitating recovery from the treatment stream and recirculation of the enzyme. The MIEX beads in normal use may be separated by an in-tank agglomeration rather than filtration mechanism (e.g., with a mixing tank followed by a settling tank, the beads then being drawn off the bottom of the settling tank), and the unit 40 of Figure 5 may be so modified when the size and flow constraints make settling a feasible or advantageous mode of recovery. Systems may also be implemented with finer particle supports such as glass or polymer beads, with or without magnetic inclusions to facilitate agglomeration. The illustrated (optional) detector may be of any suitable type for monitoring the recovery return, such as a turbidity detector, a light-based detector such as a spectral or scatter detector, a specific activity detector, or other detector. Choice of detector may depend upon the type of urease or substrate/beads (if employed) used in the treatment loop 40. Alternatively, the system may rely entirely measurements from a downstream permeate water quality detector, to control the addition of enzyme.

The present invention may advantageously be applied to treatment of water, such as pharmaceutical process water, where pyrogenic and other contaminants must be removed. The invention may also be applied to smaller flows of water than the described UPW plants. For smaller systems, immobilization on a substrate in a flow-through cartridge may readily treat the required flow volumes using materials such as yarn packing or other depth filters as described above. Membranes, activated supports and other treatment elements of the invention may also be used to retrofit existing semiconductor water plants in which neither the installed water treatment processes nor the available water quality monitoring instrumentation have fully addressed the presence of trace nitrogen organics (e.g., materials that may be present in the feed

stream or arising internally from the dead cells of system-colonizing species) in the TOC component of product water. In such cases, the invention may be practiced using other proteases, lipases or agents, or mixtures of enzymes and/or agents, that target the class of contaminants present in the particular system. When more complex treatment systems are employed, these active agents are preferably screened in pilot runs to avoid or address any adverse cross-reaction that may arise.

In addition to surface modification or immobilization of an agent on or in a conventional treatment membrane, such as an RO or a microfiltration membrane, the invention may be implemented with material immobilized on a wide variety of supports, such as porous solids, textile or yarn packings, or depth filters similar to ones used for in-line flow filtration, or on material that is itself retained in a vessel or flow cell by such porous filter material. These materials may include, for example, porous materials produced by interfacial polymerization, stretching, expansion, sintering or other processes, and may use polymers such as nylons, polysulfones, polycarbonates (including polyphthalate carbonates), PTFE, PVDF (such as the sintered products supplied by Porex Technologies, to list the materials of just one fabricator), or other compatible substrate. An example will illustrate basic steps for one such immobilization or impregnation treatment, for which a range of suitable materials are identified.

Example 1. This example describes coating/impregnating immobilized urease on a non-woven sheet substrate.

In a 400 ml beaker, beaker A, 0.25 gm urease (Sigma 4002U) was dissolved in 10 ml of 20% polyethyleneimine, (PEI) (Scientific polymer products, PEI 50% in water catalog number 135) water solution. Coupon 1, a 2.5" x 2.5" piece of Freudenberg non-woven polypropylene sheet (white color, 10 mil thick, weight: 1.78 oz/square yard) was dipped for 5 minutes. The sheet was then dried hanging vertically in a drying hood at room temperature overnight. In a separate beaker B, 250 mg of 25% glutaraldehyde water solution was dissolved and diluted to 10 ml. Coupon 1 was then dipped in beaker B for 5 minutes and was hang dried vertically at room temperature in a hood until the coupon was dry to touch. Coupon 1 changed to an amber color with some darker spots. Then the coupon was washed with two liters of Milli-Q ultrapure water. A 50 ml UPW pre-rinse water sample was filtered through coupon 1 at a flow rate of 180 ml/min

and collected and run through a urea analyzer. The UPW sample had a background reading of 1.8 ppb (as carbon) urea (this unit will be denote ppbC herein). Then a 50 ml of 17.4 ppbC standard urea solution was filtered through the coupon 1 membrane, yielding a filtered water that was then tested for urea content. The filtered water gave a 14.5 ppbc urea reading, using a urea analysis instrument supplied by Sievers Instruments. The urease immobilized on the filter sheet was thus effective to remove urea from the solution.

In general, treatment of a filter or substrate with the enzyme may be effected with two steps, optionally followed by a third step. Thus the urease (or, in general, the enzyme) immobilization formulation or procedure may employ three parts, stages or treatment components.

One part (part 1) contains the urease (or enzyme) and a binder polymer, which may, for example be selected from but is not limited to: polyethyleneimine, polyvinyl alcohol, polyvinylpyrrolidone and its copolymers, polyhexamethylene biguanide hydrochloride, polyvinyl phenol, polyacrylonitrile and its copolymers, polyvinylpyridine, polyethyleneglycol/polypropyleneglycol and its functional copolymers, polyacrylamide and its copolymers, polyvinylbenzyltrimethylammonium chloride and its copolymers, polymethylmethacrylates, its copolymers and its derivatives, polycaprolactone, and its telemers, i.e. poly(caprolactone)diol, Satomer's epoxy functional soybean oil (CN111), urethane acrylates, epoxyacrylates, polyacetal, polyvinylformal, polyvinylbutyal, polyvinylcarbazole, polyvinylbenzylchloride, cellulose, cellulose acetates, cellulose nitrate, hydroxyalkylcelluloses, starch, alginic acids sodium salt, keratin and reduced keratin, collagen, gelatine, aminal agar, seaweed agar, ethylenevinylacetate copolymers, polyethersulfone, polysulfone, polyvinylchloride, polyvinylidene fluoride, chitin, Nylon 6, Nylon6/6, Nylon 11, Nylon 12, Nafion 117, polymaleic anhydride and its copolymers, pectin, poly(vinyl methyl ether), polyvinylaniline and its copolymers, polypyrrole and its copolymers, polystyrene and its copolymers, polycarbonate, polyimides, polyimidines, Zein, poly(acrylic acid), poly(2-acrylamido-2-methylpropanesulfonic acid), polyalkyleneadipates, polydimethylsiloxane and its derivatives, poly(dimethylamino-co-epichlorohydrin) quarternized, polydimethylsilane, polybenzimidazole, polyacrylic acid and its copolymers. The enzyme and the binder co-

dissolved in a common solvent such as water, dipropylene glycol, dimethylacetamide, N-methylpyrrolidone, ketones, alcohols, propylene glycols, dimethylsulfoxane, tetrahydrofuran, and the like, with the concentration of urease range from 0.01% to 25% and the binder polymer concentration range from 0.001% to 25% by weight. The binder is not limited to using single component of the polymers named above, but can be a combination of any of the above polymer pairs or multiple components blended together in various proportions.

The second part (part 2) includes a crosslinker and a solvent. The crosslinker may be selected from: polyaldehydes, polyols, polyamine, polyoxiranes, polyhalide, polyvinyl, polyacids, cyanogen bromide, and polythio compounds. Typical crosslinking agents are glualdehyde, divinylbenzene, etc. and a solvent, with selection criteria as in part 1. The concentration of crosslinker may range from 0.001% to 100% by weight.

The immobilization technique can be practiced by mixing the formulation of part 1 and the formulation of part 2 in suitable proportions, with or without a third component (part 3) described below.

The third (optional) component (part 3) is a stabilization or treatment component. This may for example contain EDTA having a range from 0 to 4 nickel salts, a pH 7 phosphoric acid/ sodium hydroxide buffer solution, and a monomer, oligomer or polymer which, after curing (crosslinking) gives a high glass transition temperature (T_g) and high softening point to promote high temperature resistance and antimicrobial property. A filler such as mineral oxide, fumed silica, sand, short or long glass fibers, ion exchange fibers, carbon fibers, ceramic fibers, metal fibers, titanium dioxide, nickel oxide, zinc oxide, nickel boride, Raney nickel, nickel acetylacetonate, nickel acetate, nickel(II)phthalocyanine, nickel halides, nickel cyclohexanebutyrate, nickel nitrate, nickel carbonate, nickel sulfate, nickel(II) 2,9,16,23-tetraphenoxy-29H,31H-phthalocyanine, and similar macrocyclic organometallic compounds and their polymeric derivatives, zinc (II) acetylacetonate, zinc (II)phthalocyanine, zinc halides, zinc acetate, zinc(II) 2,9,16,23-tetraphenoxy-29H,31H-phthalocyanine, and similar macrocyclic organometallic compounds and their polymeric derivatives. The filler(s) may be selected to increase abrasion resistance and/or catalytic activity. This class of metal salts and metal

complexes are not limited to nickel, zinc or titanium, but may also be selected from cobalt, copper, aluminum, and magnesium salts and complexes, bucky tubes (i.e., Aldrich cat. # 40,607-4), buckminsterfullerene (i.e., Aldrich cat.# 48303-6).

All the components in part 3 are either dissolved or suspended in a solvent. Loadings may be, e.g., EDTA in the range of 0.00% to 50%, high Tg polymer or its starting material in a range from 0.00% to 50%, and the oxide filler, in a range from 0.00% to 45%. Antimicrobial materials such as polyhexamethylene biguanide hydrochloride or Microban^(tm) products (available from Microban Products Company, Huntsville, NC) can also be added to this part.

Enzyme may be applied to the substrate by one of the following processes:

1. Coating onto the bulk body, inner surface, outer surface or both surfaces of a cartridge filter module (The module may have any configuration, and all commonly employed filter materials, PP, Nylon, cotton, etc. are suitable for the enzyme treatment);
2. Coating onto one or both surfaces of a woven or nonwoven fabric, a felt or a kneaded, extruded or other screen. The fabric or other material may have a thickness range from 1 mil to 100 mils; it may, for example, take the form of a sheet, depth filter or other conventional treatment line component or structure.
3. Coating onto one or both surfaces of flat sheet MF/UF membranes, Porex sintered blocks, sheet, rod or tubule stock. The membrane material may be a material selected from polysulfone, polyethersulfone, polyvinylidene fluoride, PVC, polyacrylonitrile, polyester, polyethylene, perfluorinated PSA, Nylons, amorphous Nylons, gel and macroreticular types of membranes.
4. Using such a coated MF or other sheet to wrap around the inner or outer surfaces, or both, of a filter module. The filter module may be spiral wound or pleated, with or without spacers, and rolled up as a cartridge filter or as a spiral wound module.
5. Using chopped up chips or ground granules fabricated as a microencapsulated urease as fill in a column or a resin bottle, or mixed in an ion exchanger device, such as in filled cells of an EDI stack, a treatment tank or reactor, inside the tubule of a cartridge filter, inside the lumen of a hollow fiber module, or inside the tubule of a tubular cross-flow filtration module, to enhance urea removal efficiency.
6. Coating onto glass bead, sintered zirconium, sintered alumina, sintered stainless steel, ion exchange beads, absorber beads, activated carbon, and using the coated article to promote urea removal efficiency.

The invention may be practiced by immobilizing the material (e.g., urease) onto membranes or other supports with chemical bonding.

Urease can be immobilized onto typical microfiltration, ultrafiltration or nanofiltration membranes containing aldehyde, oxirane, hydroxyl, sulfhydryl, carboxylic acid, amine, aniline, triazine, piperazine, hydantoin, amide, imide, imidine, imidazole, pyrrolidinone, oxime, dione, pyridine, pyrrole, furan, acetal, formal, butyral, onium, sulfonate, halide, guanide, vinylidene halides, benzyl halide, silane, silanol, isocyanate, crown ethers, ferrocene, phthalocyanine, bucky tubes (i.e., Aldrich cat. # 40,607-4), buckminsterfullerene (i.e., Aldrich cat.# 48303-6), siloxane ether, phenol, and ethylenically unsaturated double bonds, by bonding/entrapping the enzyme with or without a label spacer material, such as avidin, biotin, antibody antigen, reduced keratin, substituted agarose gels, peptides, zein, collagen, amino acids, nucleotides, DNA, RNA and the like.

Advantageously, when urease is immobilized by microencapsulation within a porous medium, the medium, such as a gel, serves to protect against exposure to proteases or large molecules that might otherwise attack the urease or impair its activity. Encapsulation may also confer protection against mechanical damage, e.g., by shear forces, and may provide an environment, such as a buffered pH environment that maintains the urease molecule in a natural conformation for optimal activity. In some embodiments involving circulating urease in the feed stream ahead of an RO unit as shown in Figure 5, the retentate circulation loop of Figure 5 may be modified to form a loop that operates at high pressure using only a low-shear booster, thus avoiding multiple passes through the higher shear environment of the RO feed pressure pump. One such embodiment is described below in connection with Figure 5A.

Further, while the description herein has alluded to urease having a size of 480 kiloDaltons, or to jackbean, pigeon pea or bacterially-derived urease, these are simply understood as representing commonly available forms of commercial urease having a useful activity level. The term "urease" as used herein is also intended to encompass ureases from sources, such as fungal or other sources, as well as synthesized structural homologs of the active region of the enzyme, and the Group VIII transition metal hydrolysis catalysing agents described

above. The optimal urease for a given application may be determined by substitution and by comparison of relevant factors, such as specific activity, pH of optimum activity, half-life of bound state, activity temperature dependence, compatibility with the intended substrates or treatment processes, or other factors.

In general, both the activity level, and the overall lifetime of such urease in a bulk water treatment stream can be quite variable. Such variability stems from a number of factors. Perhaps the most widely recognized factor affecting enzyme activity is the fact that conditions such as pH, temperature and other conditions of the surrounding medium can affect the physical conformation of the enzyme molecules, thus changing the relative positions of regions or functional groups necessary for their activity. Urease is also readily decomposed by proteases commonly present in portions of a water system, and is damaged by exposure to physical trauma such as the high shear conditions of impeller-type pumps. In a bulk water system, one or more of these factors may reduce the effective lifetime of unprotected urease to under a few hours, not only affecting the basic economics or effectiveness of use but also potentially introducing excessive TOC contamination secondary to the urease destruction itself.

In accordance with another aspect of the present invention, this problem is addressed by utilizing a protected urease. Protection may take any of several forms.

One form of protection is to combine a film or surrounding medium with the urease to screen the enzyme from contacting large molecules (such as proteases). When preparing the urease, e.g., by encapsulation in a protective medium, the medium may also be compounded to inhibit loss of metal ion from the urease, and may be selected or modified to provide a protein-like surrounding that assures that the active region of the enzyme retains its natural molecular conformation and activity. For example, the protective medium may take the form of 4% cross-linked beaded agarose, or binding to other polysaccharide.

Another way of protecting urease from attack or breakdown in the practice of the present invention is to prepare the enzyme in crystalline form or cross linked enzyme crystals (CLECs), for example using the techniques of A.L. Margolin and M.A. Navin, *Protein Crystals as Novel*

Catalytic Materials Angew. Chem. Int. Ed. **2001**, 40, 2204-2222. Crystallization renders the enzyme less prone to attack by proteases, and stabilizes the molecular conformation in a generally protein-like surrounding, so that the enzyme attains a high level of activity in adverse solution environments and does not break up or lose its metal ions. While much practical CLEC work has been directed to macrocrystal (e.g., of a size comparable to chromatography media), for processes of the present invention, the CLEC material may be pulverized, or may be initially crystallized in generally smaller particles, for example below 0.1 micrometers or less. Such crystals may be used in the same manner as free enzyme, or may be encapsulated in microcapsules that can also be applied in columns or treatment tanks or loops as described above for free urease and beads. Such crystals may also be embedded in a semipermeable film or membrane, for example to form a urea-destructive thin film composite membrane or to form urea-hydrolysis surface coating of beads, membranes or screens. They may also be bonded to a functional membrane or other support, or immobilized thereon, e.g., by a glutaraldehyde or other treatment as described above, or by other methods known in the literature.

Another form such protection may take is protection from mechanical stress, such as shear stresses. While the above-mentioned crystallization, coating or encapsulation techniques offer some mechanical protection of this sort, systems of the invention may also protect a urease additive by resort to a modified system design employing treatment stages with low mechanical shear elements or interfaces, e.g., modifying a treatment subsystem so as to assure low shear conditions. Thus, as applied to the embodiment of Figure 5, mechanical shear-destruction of the urease may be avoided by the changing the free-urease high concentration recirculation loop design as shown in Figure 5A. In this embodiment, as in the treatment line of Figure 5, urease is maintained at a relatively high concentration contained within a recirculating feedback loop 60 between the retentate outlet of an RO 130 and the RO inlet, with an ultrafiltration unit 140 retaining the urease while allowing a certain level of blowdown to prevent buildup of salts and contaminants. It will be understood that in either embodiment, ultrafiltration unit 140 can be replaced by a looser filter when the urease is a crystalline, encapsulated or other form having a macro-scale dimension, e.g., a dimension appreciably larger than the molecular dimension, such as .05 –0.15 mm or other beads or microcapsules. In this embodiment, however, rather than returning to an open tank and passing again through the high pressure (and high shear) RO pump

105 to the RO unit (as occurs in Figure 5), the loop 60 of Figure 5A remains at a high pressure, returning directly to RO inlet using only a low differential pressure, low shear, pump 62 to overcome the relatively small pressure barrier of the retentate/feed pressure differential. Other treatment elements indicated generally by the numeral 61 may reside in the high pressure return loop, such as a closed tank hold-up volume (corresponding to open tank 110 of Figure 5), and the RO pump outlet 106 may connect to such tank rather than directly to the RO inlet. Suitable low-shear mechanisms for the recirculation pump 62 include piston or other such low-shear positive displacement pumps. Depending on the complexity of the recirculation portion and RO units and pressure steps present in the system, low shear elements such as pressure exchangers (diprex, DWEER, etc.) may be employed in the loop without subjecting the treatment agent to high mechanical stress or shear.

When the system employs a recirculation loop in which the concentration of urease or other active agent is maintained at a high level to enhance the removal endpoint, buffering or protective material may also be added to this loop. In this case, the unit 140 may be selected to have suitable retention properties to maintain the added material at an effective level. Such buffering or protective material may include salts and buffers common in biological uses. Applicant also contemplates that combinations of urease-specific materials, such as nickel salts and carbon dioxide, and possibly other Group VIII transition metal salts, may be introduced to preserve or re-vitiate the enzyme. Nickel and carbon dioxide have been found in other contexts to be co-factors for the assembly of urease *in-vivo*, and to prevent cleavage or promote repair of the urease molecule or its vulnerable active site, as reported in various papers of R.P. Hausinger, E. Jabri and others.

Systems of the invention that include a recirculation loop may also be arranged to operate entirely at low pressures and thus avoid mechanical trauma. For example, a system utilizing a CLEC or an encapsulated or protease-protected form of urease, or a system operating in a flow that is free of such destructive contaminants, may be configured with a holding time residence tank in the feed line before the first RO pump, and may then utilize an MF unit to retain the CLEC/urease and return it to the tank.

Systems of the invention include a number of treatment methods that are believed to represent significant advance in water treatment, applying hydrolysis or capture and/or at least partial catalytic breakdown of an organic contaminant present at only trace levels in a flow of bulk water. The integration of a circulating loop having a relatively great level of active agent, and the interconnection of treatment units by protected or low mechanical shear flow paths, in a water treatment line, and the operation of a urease portion with added salts, buffering, or metal/CO₂ urease restorative are all believed to be new and inventive advances. Other new aspects of the treatment methods and processes of the invention will be apparent from the preceding descriptions of media, treatment units and representative configurations of equipment.

In addition to operation of the invention for removal of a trace contaminant in treating bulk water for semiconductor fabrication purposes, the invention may also be practiced on other fluids, either to treat trace levels, or to reduce a substantial level of contaminant down to a low residual level. For example, treatments, and the treated media or filters of the invention may be employed in fluid flow treatment systems for regeneration of kidney dialysate, for treatment of pharmaceutical manufacturing process water, for treatment of certain waste waters, and for other treatment applications.

As regards the treatment of UPW fabrication plant water, several additional aspects of the invention bear noting here. First, the initially-observed outbreaks of urea-induced wafer defects resulted from urea levels that were not detected by a standard TOC detector, and that were already quite low. Much urea had been effectively removed from the feed water via the normal treatment processes. This suggests that if the urea removal efficiency of the upstream processes were better, then the residual urea, even though not detected and quantified, might have been sufficiently low to avoid adverse effects without a later trace removal step. The problem is attacked in one aspect of the invention by a front-end treatment of consciously modifying an upstream or early treatment stage to specifically reduce the level of a high input urea concentration by a factor of at least two – for example, by 50-99%; preferably above 70 or 80 %, and most preferably in the range of 85-99%. Applicant has determined that this may be accomplished by judicious selection of the type of RO membrane employed in an upstream position. For example a Toray UTC-80 seawater RO membrane has high urea rejection. It is

believed that the (usually reported) boron rejection level of an RO membrane will correlate well with its urea rejection, due to the similarity of their respective molecular size and other properties, so that characteristic may be employed as a guide in initially selecting suitable candidate membranes for such front-end low urea treatment processing. In accordance with this aspect, by optimizing front-end treatment of the feed stream to limit passage of urea to the later stages, any spike in urea present in the feed is strongly attenuated after early stage treatment.

Another factor to note, in embodiments intended for semiconductor UPW fab water production where the level of urea (and of TOC generally) is to lie below a low limit, is that the route initially identified for introduction of urea-mediated wafer defects was use of the UPW product in a plant humidification system. Apparently this produced nitrogen-bearing particulate contamination, leading to production of ammonia that locally inhibited the acid-catalyzed developer chemistry. The problem of urea concentration and dispersal via humidifiers is addressed in accordance with another aspect of the invention by providing product water to a non-spray-type humidifier, for example a humidifier operating by evaporation from a wetted web, so that aerosols (and particles resulting from the drying of aerosols) are not formed, or such that the urea/organic contaminant does not enter the humidified air. Urea may then be permitted to pass at higher levels in the product, without introducing concentrated urea droplets or particulates into the air.

Thus, in addition to directly addressing a trace level of contaminant. The invention includes a number of different approaches to assuring that product water has a more attenuated level than heretofore, or that downstream water use (particularly humidification) is modified to block the contaminant from acting.

The invention being thus disclosed and illustrative embodiments described, further variations and modifications within the scope and spirit of the invention will occur to those skilled in the art, and all such variations and modifications are considered to be within the invention as defined herein and in the claims appended hereto.

CLAIMS:

1. A high-purity water production apparatus comprising a pretreatment unit and a deionization unit for respectively removing suspended solids and removing ions, operating on a treatment stream to produce a high purity product water, wherein

said deionization unit includes at least one unit selected from the group consisting of an RO unit, an electrodialysis or electrodeionization unit, and a distillation unit; and wherein

the apparatus includes a trace organic nitrogen removal unit for contacting the treatment stream with said removal unit effective to cleanse a trace organic nitrogen contaminant from the stream to a level below 10 ppb as nitrogen, and preferably below 0.5 ppb as nitrogen.

2. The apparatus of claim 1, wherein the removal unit includes a high flow substrate having an immobilized enzyme, the enzyme being selective for said trace organic nitrogen contaminant.

3. The apparatus of claim 2, wherein said substrate is a semipermeable membrane.

4. The apparatus of claim 1, wherein the removal unit includes a direct capture membrane or resin functionalized to remove the trace organic nitrogen contaminant by covalent attachment.

5. The apparatus of claim 4, wherein the direct capture membrane or resin is functionalized to at least partly break down the trace organic nitrogen contaminant into a captured moiety and a removable moiety, and the removable moiety is removed from the treatment stream by a treatment element of the apparatus.

6. The apparatus of claim 1, wherein the removal unit includes an affinity resin or a resin having polymer-bound ketone, diketones, amine, hydrazine, hydrazide, and/or aldehyde groups.

7. The high-purity water producing apparatus of claim 1 or 2, wherein the removal unit includes a membrane or resin functionalized to bind urease, and further includes urease immobilized thereon, OR wherein the removal unit includes a membrane or resin functionalized to contain a coordinated nickel complex or other group 8 transition metal complexing agent thereon.
8. The apparatus of claim 7, wherein the removal unit includes a filter element selected from the group of elements consisting of a hollow microporous tubule, a solid microporous tubule, a cartridge filter with pleated membrane sheets or winded span yarn, a flow-through column containing particles or beads, a spiral wound activated-nonwoven sheet, and a spiral wound or hollow fiber microfiltration module having a treated surface.
9. The water producing apparatus of claim 1, wherein the removal unit includes a feeder for injecting urease into the stream, and optionally includes a tank or mixing portion for raising contact time of the stream and the injected urease.
10. The water producing apparatus of claim 9, further comprising a recovery loop for recovering and returning urease to the stream whereby an elevated concentration is maintained in a removal portion of a treatment plant.
11. The high-purity water producing apparatus of claim 9, further comprising a detector operative to detect said contaminant at said trace level, and a controller operative to operate the feeder in response to said detection so as to reduce the trace level below a desired threshold.
12. The high-purity water producing apparatus of claim 1, 2, 6 or 7, wherein the removal unit contacts the stream upstream of a deionizer or a degasifier.

13. The high-purity water producing apparatus of claim 1, 2, 6, or 7, wherein the removal unit resides in a polishing loop.

14. The high-purity water producing apparatus of claim 1, wherein the removal unit is constituted with a cartridge polisher.

15. The apparatus of claim 1, wherein the removal unit includes a sacrificial medium situated in a downstream position of a UPW treatment line.

16. The apparatus of claim 1, wherein the removal unit includes a bound enzyme medium situated in an upstream position of a UPW treatment line.

17. An improved UPW treatment system for high volume production of ultra high purity water, wherein the improvement comprises a treatment unit for contacting the water and effective to capture or break down a trace organic nitrogen impurity to produce ultra high purity water having said trace organic impurity present at a level below ten and preferably below about one ppb.

18. The improved UPW system of claim 17, wherein said treatment unit includes a solid element having an active material surface-immobilized thereon, and said system contacts the water to a surface of said element.

19. The improved UPW system of claim 17, wherein said active material is a material selected from among the group of materials consisting of an enzyme, a capture material, an organometallic reaction material and combinations thereof.

20. The improved UPW system of claim 18, wherein said solid element is an element selected from the group consisting of particles, semi-permeable membranes, other semi-permeable media, and combinations thereof.

21. The apparatus of claim 1, wherein the removal unit includes an active medium effective to cleave said organic nitrogen contaminant into components and an EDI unit operable to removed said components from the treatment stream.

22. Treatment apparatus for producing ultrapure water, wherein the apparatus includes a removal unit for removing a target organic nitrogen contaminant present in a treatment stream at low concentration, by directly surface contact of the flowing treatment stream with an active material.

23. A water treatment element comprising a substrate material having an activated surface effective to remove a contaminant present at trace level in a treatment stream by direct contact with said stream.

24. A water treatment system for production of ultra high purity water and comprising a plurality of treatment units arranged to remove impurities from a stream of feed water to produce a product water, e.g., primary make up water, substantially free of impurities, and characterized by including a high flow contact element in the treatment stream effective to remove trace level of urea contaminant from the stream.

25. Apparatus for water treatment, comprising a cross flow membrane water treatment element having an enzyme or agent immobilized on its membrane effective to remove a target contaminant form water treated by said treatment element.

26. Apparatus for water treatment, comprising a a plurality of water treatment units arranged in a water treatment line including a reverse osmosis (RO) unit, a low shear recirculation loop returning at least a portion of RO retentate to an inlet of said RO unit, and a urea removal material in said recirculation loop effective to urea from water in said treatment line.

27. Material for water treatment, the material comprising a microparticle substrate having an

immobilized enzyme or agent such that said material is effective to remove a target contaminant from water by injection of said material in the water, and the substrate is recoverable for recovery and reuse in at least a portion of a water treatment line.

28. The material of claim 27, wherein said substrate includes magnetic material for enhancing separation of the substrate from the water.

29. The material of claim 27, wherein said portion includes a treatment tank and recovery is effected as retentate of a filtration unit, said portion operating as a substrate circulation loop whereby an elevated concentration of said enzyme or agent is maintained in said portion of the water treatment line.

30. The material of claim 27, wherein the immobilized enzyme is a crystal or cross linked crystal.