

METHOD OF VAPORIZING LIQUIDS BY MICROWAVE HEATINGField of the Invention

This invention is generally related to a method
5 for purifying saturated liquids. More specifically,
this invention is related to a method for purifying
saturated liquid using microwave energy during the
vaporizing process to produce ultra high purity gases.

Background of the Invention

10 Process gases for use in semiconductor
manufacturing facilities are generally supplied through
cylinders. In order to meet the increasing demand for
high flow rate product and ultra-high purity
requirements for these gases, gas producers often use
15 an ultra-high purity bulk vaporizer delivery system to
treat polar liquefied compressed gases. In general,
the on-site system uses a microwave source of energy to
increase and to control the evaporation rate of aqueous
polar liquids (such as ammonia). The on-site system is
20 able to provide purification, short response time, and
accurately controllable vaporization at very high flow
rates (exceeding 1000 liters/min in large volumes for
the semiconductor industry). To sustain the
vaporization of the polarized liquidified compound,
25 energy must be added to the system to replace the heat
that is carried off with the gaseous flow to the
customer use point. If this is not done, the
temperature in the gas will drop and the polar liquid's
vaporization rate will decrease until the gas-liquid
30 pool eventually sub-cools and all vapor flow cease.

If the liquefied gases require additional
purification, the vaporizer system can reduce the



- 2 -

amount of impurities that is introduced into the vapor phase, thus adding a purification step. The impurities that will be excluded from the vapor phase and remain in the liquid pool as a result of liquid evaporation includes Group I, Group II and Group III metals, as well as oxides, carbonates, hydrides and halides of these elements. These impurities come from a number of sources including friction from valves actuation, thermal expansion and contraction of liquid containers, pressure stretch or expansion on vessel container openings during filling, etc. Moisture is another source of impurity. Based on vapor-liquid equilibrium data, the concentration of moisture in the liquid phase is approximately 2 to 3 times greater than the concentration in the vapor phase. Careful handling in evaporating the liquid phase to the vapor phase can reduce moisture and other non-volatile residues (NVR) by orders of magnitude.

A common practice for delivering purified gas is through the vaporizer approach, which uses electrical-resistance heating. The process withdraws vapor from a tank and heats it with a heat source from either an internal heater or external band heaters to provide heat in excess of available ambient heat. The vapor then passes through a heat exchanger with the pool of non-cryogenic liquefied compressed gas to promote further vaporization in the tank. Conduction and convection transfer the heat to the bulk liquid from a line source, which increases the system response time. The use of immersion heaters or shell and tube heat exchangers can release particulate and act as a nucleation source for boiling of impurities like

- 3 -

moisture, since the nucleation source is substantially hotter than the bulk liquid. Agitation promotes boiling as gradients and nucleation sites are generated. Agitation also increases the mobility of non-volatile residues (NVR), increasing the chances of allowing passage into the vapor phase.

U.S. Patent No. 4,671,952 discloses a process and apparatus for generating sulfur dioxide vapor from contaminated liquid sulfur dioxide. The process uses contaminated liquid sulfur dioxide and subjecting it to microwave energy at a frequency of 915, 2450, 5850, or 18000 Mhz for a sufficient period of time to produce sulfur dioxide vapor, collecting the vapor and removing the resulting contaminated liquid sulfur dioxide, if any. The vapor pressure of the sulfur dioxide is 34.4 psig at 70 °F and purity of sulfur dioxide achieved is 98.99%.

U.S. Patent No. 4,285,774 discloses an apparatus that continuously produces concentrated alcohol from beer. A plurality of concentrator cells and a plurality of salvage cells are arranged in a line in side-by-side relation. Beer is supplied to the first upstream concentrator cell through a supply conduit. The beer then flows through passages between adjacent cells in response to the volume of beer reaching a predetermined level in the adjacent upstream cell. A microwave ignition bulb is positioned in each cell to heat the beer and boil or vaporize the alcohol content. The gaseous alcohol serially bubbles through a fluid passage from each concentrator cell to the next adjacent upstream cell until the gaseous alcohol reaches the first concentrator cell where the gaseous

- 4 -

alcohol is concentrated and condensed in a column to a liquid solution containing approximately 95% alcohol and approximately 5% water. The alcohol obtained from the dilute, substantially spent beer in the salvage
5 cells is collected and returned to the supply conduit for recycle.

U.S. Patent No. 5,882,416 discloses a liquid delivery system for delivering a liquid reagent in vaporized form to a chemical vapor deposition reactor.
10 The reactor is arranged in a vapor-receiving relationship to the liquid delivery system. The liquid delivery system includes an elongated vaporization fluid flow passage defined by a longitudinal axis and bounded by an enclosing wall. A vaporization-heating
15 element contained within the fluid flow passage transverse to the longitudinal axis for heating the fluid to vaporization. The vaporized liquid is then carried to a chemical vapor deposition reactor.

U.S. Patent No. 5,846,386 discloses an on-site
20 vaporizer that draws ammonia vapor from a liquid ammonia reservoir. The ammonia vapor then passes through a microfiltration filter, and is then scrubbed using high-pH purified water. Commercial grade ammonia converts to sufficiently high-purity ammonia without
25 the need for conventional column distillation. Liquid ammonia is stored in a reservoir. An external immersion heat source draws vapor from the vapor in a liquid ammonia supply reservoir that serves as a single stage distillation, leaving certain solid impurities
30 and high-boiling impurities behind in the liquid phase. The ammonia vapor drawn from the vapor space in the reservoir passes through a microfilter. A pressure

- 5 -

regulator controls the flow of the filtered vapor and directs it to a scrubbing column/circulation pump combination and then to either a distillation column, a deionized water dissolving unit for purified liquid product point of use, or to transfer lines for gaseous point of use. The vapor headspace of the reservoir controls the flow rate. Microwave energy rapidly replaces the energy loss to the proposed microwave system. A circulation pump is employed in the microwave vaporizer/evaporator system, which can be a source of metallic impurities.

U.S. Patent No. 5,523,652 discloses using microwave energy in a dielectric plasma chamber, a pair of vaporizers, a microwave tuning and transmission assembly and a magnetic field generating assembly. The chamber defines an interior region in which a source gas is routed and ionized to form plasma. The microwave tuning and transmission assembly feeds microwave energy to the chamber in the TEM mode.

None of the prior art is believed to teach or suggest using microwave energy to control vaporizing a saturated liquid below its boiling point and produce ultra high purity gases.

Summary of the Invention

An aspect of this invention is directed to a method for separating a polar liquid comprising a) introducing an effective amount of microwave energy at a depth of up to about 30 mm into the liquid below the surface of the liquid; b) controlling the microwave energy that is introduced into the liquid to maintain a temperature below the boiling point of the liquid; c) evaporating the liquid in the presence of the microwave

- 6 -

energy while sustaining the temperature below the boiling point of the liquid to form purified vapors; and d) capturing the evaporated purified vapors.

Another aspect of this invention is directed to a method for separating a polar liquid comprising introducing microwave energy at a depth of up to about 30 mm into the liquid below the surface of the liquid to reach the liquid's boiling point; controlling the microwave energy to near the boiling point of the liquid; evaporating the liquid in the presence of the microwave energy while sustaining the temperature below the boiling point of the liquid to form purified vapors; and capturing the evaporated purified vapors.

The microwave energy is introduced to a temperature of up to about 5°C above the boiling point of the liquid by controlling the vapor pressure of the liquid.

The resulting purity of the purified liquid is less than 1 ppm of impurities.

Brief Description of the Drawings

Other objects, features and advantages will occur to those skilled in the art from the following description of preferred embodiments and the accompanying drawing, in which Fig. 1 provides a schematic diagram of the storage, evaporation and delivery method in this invention.

Detailed Description of the Invention

This invention uses impure polar liquid (i.e., ammonia) and add heat thereto to vaporize the polar liquid while obtaining higher purity in the vapor phase. This ensures that heat addition is done slowly. Microwave radiation is used to maintain the temperature

- 7 -

of the polar liquid pool below the boiling point of the polar liquid at that pressure. Boiling or agitation of the polar liquid does not generally take place.

However, it is preferable to apply sufficient microwave energy to reach the boiling temperature of the polar liquid, and then to adjust the microwave energy to below the boiling point of the polar liquid, but enough microwave energy to vaporize the polar liquid. It is believed that this use of microwave energy to purify polar liquid maintains its purity for two reasons. First, minimizing agitation, which would occur in the system if boiling is kept to a minimum, keeps the impurities at the bottom of the liquid pool where vaporization is not occurring. Second, moisture, organic oils, and non-volatile residues prefer to remain in the liquid phase of the polar liquid. Second, moisture, organic oils and non-volatile residues prefer to remain in the liquid phase of the polar liquid. The invention prevents the system from boiling by maintaining the temperature below the boiling point of the polar liquid. This ensures a careful vapor phase transfil in that the moisture, organic oils and non-volatile residues remain in the liquid phase without transferring into the vapor phase. If the polar liquid is allowed to boil at an extended period, some of the moisture, organic oils and non-volatile residues would be able to transfer (in large concentrations) to the vapor phase by the agitation. Ultimately, the invention is able to produce vapor ammonia with parts per billion impurity levels.

Microwave energy replaces the energy that is lost from evaporation, while maintaining the vapor-liquid

- 8 -

equilibrium in the vessel. As the liquid in the vessel evaporates and the vapor flow increases, the vapor pressure drops. Also, as the liquid evaporates and the liquid in the vessel evaporates, the temperature drops and the liquid subcools. The pressure drop also prevents spot boiling. The microwave energy maintains the appropriate pressure and temperature equilibrium, thereby maintaining the evaporation rate and energy in the system.

One method of operation is to run the process in a batch mode. The polar liquid is allowed to decrease to a certain level, and then turn the microwave off, while the vessel will subsequently be refilled with the polar liquid. Another method of operation is through continuous addition of polar liquid while the microwave energy is applied.

Spot boiling may occur as the evaporated polar liquid is drawn off the top of the vapor fill. This decreases the pressure. Also, as the polar liquid is drawn off the top of the vapor fill, the temperature of the liquid drops causing the liquid to subcool. The subcooled liquid will spot boil at the reduced vapor pressure. The microwaves energy replaces the heat and pressure loss of the system to reestablish the vapor-liquid/pressure temperature equilibrium. The equilibrium of the vessel is at a temperature below (but very close to) the boiling point for that pressure. By reestablishing this equilibrium, the invention operates to prevent spot boiling of the polar liquid.

The benefits for using microwave energy as a source of heat includes: 1) rapid response to rapid

- 9 -

heat of vaporization energy replacement to avoid boiling ammonia in liquid pool; 2) absence of particulate contamination; and 3) efficient energy use. Microwave energy sources are very efficient for heating polar substances, where the positive and negative charge centers are separated in space even though the net charge on the molecule is zero. Thus, in polar substances like water or in ammonia, the charge separation enables coupling of the molecules to the energy, thus resulting in heating.

Microwave energy, when delivered into a tank holding a liquid, will penetrate the liquid to a depth depending on the permittivity, permeability, and microwave mode of operation, to heat volume layer. As the surface recedes by evaporation, further layers get heated. Since the heating element is the liquid itself, when the power is turned off, heating ceases instantly, resulting in "rapid response".

Microwave energy is delivered through a wave-guide and a quartz window. There is little or no contamination because the energy is delivered without contact with any nucleation source for boiling other impurities.

Volumetric heating produces high efficiency because it does not depend on conduction and convection to a great extent. Further, because the penetration depth is estimated at up to about 30 mm, preferably between about 16 mm to 20 mm, the volume of gas reaching the freeboard in the tank by evaporation is heated.

In order to satisfy the need for safe cost effective bulk source and delivery system, the present

- 10 -

invention provides a method and apparatus for delivering ultra high purity polar and non-polar process gases. The delivery system is an evaporation system capable of sustaining a high flow rate. The
5 evaporation system contains a large quantity of polar and non-polar saturated liquid chemical product where the chemical has at least a vapor phase and a liquid phase.

Vapor-liquid equilibrium data for the trace
10 moisture-ammonia system may be generated. Most of the moisture reside in the liquid phase. The concentration of moisture in the liquid phase is approximately 2 to 3 orders of magnitude greater than the concentration in the vapor phase. A similar distribution between phases
15 of trace oils and other non-volatile residues (NVR) has been observed. Based on the vapor-liquid equilibrium data using the Smolen publication, the vapor phase moisture may be reduced by evaporating or distilling the ammonia from the liquid phase to a vapor phase,
20 sometimes known as a "vapor phase transfill".

Careful vapor phase transfill can reduce moisture content by two orders of magnitude, i.e., from 100 ppm to less than 1 ppm. This purification is only achieved when the flow rate of the transfill is carried out
25 slowly enough to prevent rapid boiling of the liquid ammonia. If boiling occurs, no purification will be accomplished, as all the moisture in the liquid phase will simply vaporize into the gas phase. However, a low flow gas phase transfill will allow the system to
30 maintain the favorable vapor-liquid equilibrium moisture distribution and produce a two order of magnitude moisture concentration reduction. A similar

- 11 -

reduction in vapor phase oil and NVR concentration will occur at the same time.

To maintain the slow rate of evaporation, energy must be added to the system to replace the heat
5 required for vaporization. If this is not done, the temperature of the system will drop, the rate of evaporation will decrease, and the ammonia will begin to boil. As a result, all purification advantage for moisture, oils and NVR will be lost. A standard
10 evaporator approach using internal or external heaters with agitation tends to promote boiling by generating gradients and nucleation sites. Agitation also increases the mobility of NVR, thereby increasing the chances of passage into the vapor phase.

15 The current invention uses microwave heating to correct the amount of controllable energy needed to sustain the evaporation process.

In the practice of this invention, vaporized product is withdrawn from the top of the evaporator,
20 the vapor having a lower concentration of impurities than the compressed liquid phase. The microwave source causes the liquid to evaporate. Microwave heating of polar liquid is based on the premise that the positive and negative charges are not coincident in space.
25 Consequently, the molecules have a tendency of orienting themselves in response to the electric field. However, the electric field in the microwave region of the electromagnetic spectrum oscillates at a rate that far exceeds the movement of the molecules. This
30 creates an internal resisting force, which interacts with the electric field and generates heat. The precise microwave frequency for this type of viscous

- 12 -

heating is not important. What is important, however, is that just enough internal friction is generated by the electric field of the electromagnetic wave to increase the vapor pressure of the saturated liquid to
5 sustain a required flow rate to the customer.

Turning now to Fig. 1, which provides for a schematic depiction of the storage, evaporation and delivery method for this invention. Also included is a gravity-fed withdrawing system which feeds saturated
10 liquid product. For purposes of this invention, the saturated liquid products may include, but not limited to NH_3 , HF , SiHCl_3 , SiH_2Cl_2 , C_4H_8 , C_3F_8 , HBr , C_5F_8 , ClF_3 and TEOS. The saturated liquid products are fed in ton containers 1 and 5, which are set on scales 2 and 6.
15 Line purging includes separate ESO panels 3 and 7 and nitrogen purge-panel for line-purging. Product ton containers 1 and 5 include ESO 3 and 7 with isolation solenoid valves 11 and 15, level control valves 12 and 16, as well as check valve 17 and manual isolation 18
20 to permit liquid products 38 and 39 to be introduced into microwave evaporator 19. The amount of product in the evaporator is monitored by level transmitter 13 and controlled by a combination of level controller 14, level control valves 12 and 16, feedback from scale
25 value 2 and 6, and isolation valves 11 and 15. Once the evaporator is filled to a certain level, control valves 12 and 16 are closed. The microwave power supplies and magnetron 21 is turned on. The microwave unit is capable of supplying a high number of wafts and
30 its duty cycle is controlled by the combination of a reverse acting pressure controller and reverse acting temperature controller via a low selected signal. The

- 13 -

microwave power supply and magnetron operate at 2.45 Ghz.

Multi-mode microwaves generated by magnetron 21 conducted down wave guide 22 are introduced into the evaporator by way of symmetric plasma coupler or E-bend 23 in such a way that the electric field vector E lies entirely within the plane of incidence to the vapor-liquid interface and is parallel polarized.

The incident wave that approaches the plane vapor-liquid interface between the two phases result in a transmitted wave in the liquid media and a reflected wave in a first media. There will be some reflection, which will combine with the incident wave and produce a standing wave, however, the reflection will be very small. Ammonia is a dielectric, therefore, the electric field and magnetic field depth of penetration into liquid ammonia will be from about 16 mm to about 20 mm at a temperature of from about 20°C to about 40°C. Upon heating, about 16 mm to about 20mm layers of ammonia will evaporate. Product vapor is withdrawn through flow orifice 31 and flow limit control valve 34, which is controlled by reverse acting flow controller 33. The evaporator product is sampled at position 35, and analyzed at analyzer 36. Automatic shutoff mechanism 37 will trigger if product purity falls outside designated limits. The current invention provides that the product flow to customer battery limits at a rate of approximately 1000 l/min. This is accomplished by maintaining the thermal equilibrium between the liquid vapor phase. The PID control loops which controls the microwave energy can rapidly respond

- 14 -

to the need for maintaining steady vapor pressure by replenishing heat to the system loss by high flow rate.

This invention maybe operated using any polar saturated liquids, however, for purposes of this invention, particularly interested saturated liquid may include, but are not limited by NH_3 , HF , SiHCl_3 , SiH_2Cl_2 , C_4H_8 , C_3F_8 , HBr , C_5F_8 , ClF_3 , TEOS and the like. The frequency chosen for this device is 915, 2450, 5850, and 18000 MHz. Flow rates from 1 to 1000 l/min or higher can be achieved by this process with moisture and NVR levels less than about 1 ppm. Contaminants which remain in the liquid pool can be continuously dumped with continuous filling or periodic dump. The system's performance is optimized by integrating a geometric shape with multiple magnetrons located surrounding liquid volume on a specially designed shape. This may reduce the number of microwave interference pattern that can create spot focusing and uneven heating.

Specific features of the invention are shown in one or more of the drawings for convenience only, as each feature may be combined with other features in accordance with the invention. Alternative embodiments will be recognized by those skilled in the art and are intended to be included within the scope of the claims.

- 15 -

What is claimed is:

1. A method for separating a polar liquid comprising

5 a) introducing an effective amount of microwave energy at a depth of up to about 30 mm into the liquid below the surface of the liquid;

b) controlling the microwave energy that is introduced into the liquid to maintain a temperature
10 below the boiling point of the liquid;

c) evaporating the liquid in the presence of the microwave energy while sustaining the temperature below the boiling point of the liquid to form purified vapors; and

15 d) capturing the evaporated purified vapors.

2. The method of claim 1 wherein said introducing microwave energy to a temperature up to
20 about 5°C above the boiling point of said liquid.

3. The method of claim 1 comprising controlling the vapor pressure of the liquid.

25 4. The method of claim 1 further comprising applying microwave energy at a frequency between 915 MHz to 18000 MHz.

5. The method of claim 1 comprising maintaining
30 the microwave energy that is introduced into the liquid to evaporate the liquid at a flow rate between 1 to 1000 l/min.

- 16 -

6. A method for separating a polar liquid comprising

- a) introducing microwave energy at a depth of up to about 30 mm into the liquid below the surface of the liquid to reach the liquid's boiling point;
- b) controlling the microwave energy to near the boiling point of the liquid;
- c) evaporating the liquid in the presence of the microwave energy while sustaining the temperature below the boiling point of the liquid to form purified vapors; and
- d) capturing the evaporated purified vapors.

7. The method of claim 6 wherein said introducing microwave energy to a temperature up to about 5°C above the boiling point of said liquid.

8. The method of claim 6 comprising controlling the vapor pressure of the liquid.

9. The method of claim 6 further comprising applying microwave energy at a frequency between 915 MHz to 18000 MHz.

10. The method of claim 6 comprising maintaining the microwave energy that is introduced into the liquid to evaporate the liquid at a flow rate between 1 to 1000 l/min.