

UNITED STATES PATENT AND TRADEMARK OFFICE

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BEFORE THE PATENT TRIAL AND APPEAL BOARD

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BASF CORPORATION,  
Petitioner,

v.

ENTHONE, INC.,  
Patent Owner.

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Case IPR2016-00697  
Patent 7,815,786 B2

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Before KEVIN F. TURNER, SHERIDAN K. SNEDDEN, and  
KEVIN W. CHERRY, *Administrative Patent Judges*.

SNEDDEN, *Administrative Patent Judge*.

FINAL WRITTEN DECISION  
35 U.S.C. § 318(a); 37 C.F.R. § 42.73

## I. INTRODUCTION

This is a Final Written Decision in an *inter partes* review challenging the patentability of claims 1–6, 8, and 11–18 of U.S. Patent No. 7,815,786 B2 (Ex. 1001; “the ’786 Patent”). We have jurisdiction under 35 U.S.C. § 6. We conclude for the reasons that follow that Petitioner has shown by a preponderance of the evidence that claims 1–6, 8, and 11–18 of the ’786 patent are unpatentable.

### A. Procedural History

BASF Corporation (hereinafter, “BASF”) filed a corrected petition (Paper 4, “Pet.”) requesting *inter partes* review of claims 1–6, 8, and 11–18 of U.S. Patent No. 7,815,786 B2 (“the ’786 Patent”). Patent Owner Enthone, Inc. (“Enthone”) filed a Preliminary Response (Paper 8, “Prelim. Resp.”). Based on these submissions, we instituted trial on the following grounds of unpatentability asserted by Petitioner:

| Basis | References                                                               | Claims            |
|-------|--------------------------------------------------------------------------|-------------------|
| § 103 | Barstad, <sup>1</sup> Alling, <sup>2</sup> and BASF Catalog <sup>3</sup> | 1–6, 8, and 11–18 |
| § 103 | Morrissey, <sup>4</sup> Alling, and BASF Catalog                         | 1–6, 8, and 11–18 |

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<sup>1</sup> Ex. 1003, Barstad et al., US 6,444,110 B2, issued, Sept. 3, 2002 (“Barstad”).

<sup>2</sup> Ex. 1006, Alling et al., US 2002/0127847 A1, published Sept. 12, 2002 (“Alling”).

<sup>3</sup> Ex. 1005, BASF, Pluronic and Tetronic Surfactants (1989) (“BASF Catalog”).

<sup>4</sup> Ex. 1004, Morrissey et al., US 2002/0043467 A1, published Apr. 18, 2002 (“Morrissey”).

Decision to Institute (Paper 10, “Dec.”).

After institution of trial, Patent Owner filed a Patent Owner Response (Paper 17, “PO Resp.”), to which Petitioner filed a Reply (Paper 20, “Reply”).

Petitioner relies on the Declarations of Bruce Pound, Ph.D. (Ex. 1002 and Ex. 1029) and Christopher G. Utz (Ex. 1021) in support of the proposed grounds of unpatentability.

Patent Owner relies on the Declaration of Dale Barkey, Ph.D. (Ex. 2031).

Oral argument was conducted on May 10, 2017. A transcript is entered as Paper 30 (“Tr.”).

*B. The '786 Patent (Ex. 1001)*

The '786 Patent relates to a method for electrolytically plating copper onto a substrate having submicron-sized interconnect features using a source of copper ions and suppressor compound having polyether groups.

Ex. 1001, Abs. The '786 Patent discusses known systems that rely on so-called “superfilling” or “bottom-up growth” to deposit copper into high aspect ratio features, where the superfilling involves rapid bottom-up deposition at a superfill speed, rather than at an equal rate on all its surfaces, to avoid seams and pinching off that can result in voiding. *Id.* at Abstract, 2:16–21.

The '786 Patent discloses a suppressor compound formed from a combination of propylene oxide (PO) repeat units and ethylene oxide (EO) repeat units present in a PO:EO ratio between about 1:9 and about 9:1 and bonded to a nitrogen-containing species, wherein the molecular weight of

the suppressor compound is between about 1000 and about 30,000. *Id.* at 3:25–39.

*C. Challenged Claims*

Independent claim 1 and dependent claims 2–6, 8, and 11–18 are challenged by BASF in its Petition. Claim 1 is illustrative and is reproduced below:

1. An electrolytic plating composition for electrolytically plating Cu onto a semiconductor integrated circuit substrate having a planar plating surface and submicron-sized interconnect features by immersion of the semiconductor integrated circuit substrate into the electrolytic solution, the composition comprising:

a source of Cu ions in an amount sufficient to electrolytically deposit Cu onto the substrate and into the electrical interconnect features; and

a suppressor comprising a compound selected from the group consisting of:

(i) a first suppressor compound comprising a polyether group bonded to a nitrogen-containing species, wherein the polyether group comprises a combination of propylene oxide (PO) repeat units and ethylene oxide (EO) repeat units present in a PO:EO ratio between about 1:9 and about 9:1, and wherein the molecular weight of the first suppressor compound is between about 1000 and about 3600 g/mol;

(ii) a second suppressor compound comprising a polyether group bonded to a nitrogen-containing species, wherein the polyether group comprises a combination of propylene oxide (PO) repeat units and ethylene oxide (EO) repeat units present in a PO:EO ratio between about 1:9 and about 9:1, wherein the molecular weight of the second suppressor compound is between about 1000 and about 30,000 g/mol, and wherein the second suppressor compound further comprises a capping moiety selected from the group consisting of an alkyl group or a block

polymer comprising propylene oxide repeat units;

(iii) a third suppressor compound comprising a polyether group bonded to a nitrogen-containing species, wherein the polyether group comprises a combination of propylene oxide (PO) repeat units and ethylene oxide (EO) repeat units present in a PO:EO ratio between about 1:9 and about 9:1, wherein the nitrogen-containing species is an alkylether amine, and wherein the molecular weight of the third suppressor compound is between about 1000 and about 30,000 g/mol; and

(iv) a fourth suppressor compound comprising a polyether group bonded to a nitrogen-containing species, wherein the polyether group comprises a combination of propylene oxide (PO) repeat units and ethylene oxide (EO) repeat units present in a PO:EO ratio between about 1:9 and about 9:1, wherein the molecular weight of the fourth suppressor compound is between about 1000 and about 30,000 g/mol, and wherein a nitrogen in the nitrogen-containing species is a quaternary amine;

(v) a fifth suppressor compound comprising a polyether group bonded to a nitrogen-containing species, wherein the polyether group comprises a combination of propylene oxide (PO) repeat units and ethylene oxide (EO) repeat units present in a PO:EO ratio between about 1:9 and about 9:1, wherein the molecular weight of the fifth suppressor compound is between about 1000 and about 30,000 g/mol, and wherein the composition comprises less than about 30 g/L acid when the fifth suppressor is selected;

(vi) a sixth suppressor compound comprising a polyether group bonded to a nitrogen-containing species, wherein the polyether group comprises a combination of propylene oxide (PO) repeat units and ethylene oxide (EO) repeat units present in a PO:EO ratio between about 1:9 and about 9:1, wherein the molecular weight of the sixth suppressor compound is between about 1000 and about 30,000 g/mol, and wherein the composition comprises between about 4 g/L and about 30 g/L copper ion when the sixth suppressor is selected; and

(vi) combinations thereof.

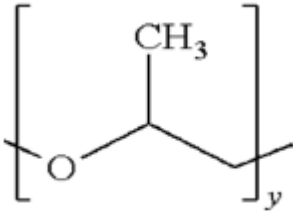
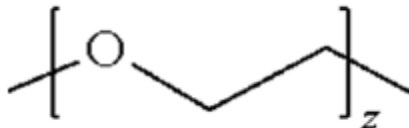
## II. ANALYSIS

### A. Claim Construction

We interpret claims using the “broadest reasonable construction in light of the specification of the patent in which [they] appear[.]” 37 C.F.R. § 42.100(b); see *Cuozzo Speed Techs., LLC v. Lee*, 136 S. Ct. 2131, 2144–46 (2016). Under that standard, claim terms generally are given their ordinary and customary meaning, as would be understood by one of ordinary skill in the art in the context of the entire disclosure. *In re Translogic Tech., Inc.*, 504 F.3d 1249, 1257 (Fed. Cir. 2007). “Absent claim language carrying a narrow meaning, the PTO should only limit the claim based on the specification . . . when [it] expressly disclaim[s] the broader definition.” *In re Bigio*, 381 F.3d 1320, 1325 (Fed. Cir. 2004) (citation omitted). “Although an inventor is indeed free to define the specific terms used to describe his or her invention, this must be done with reasonable clarity, deliberateness, and precision.” *In re Paulsen*, 30 F.3d 1475, 1480 (Fed. Cir. 1994).

In our Decision to Institute, we adopted constructions for the terms “suppressor,” “superfill”, and “propylene oxide (PO) repeat units” as provided in the table below.

| Claim term                          | Adopted Construction                                                                                                                               |
|-------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------|
| “suppressor”                        | compound that inhibits electrolytic plating and facilitates superfilling of features in a system having an accelerator                             |
| “superfill”                         | filling a feature from the bottom up, rather than at an equal rate on all its surfaces, to avoid seams and pinching off that can result in voiding |
| “propylene oxide (PO) repeat units” | the chemical structure represented by the formula $C_3H_6O$ with the following structure                                                           |

|                                    |                                                                                                                                                                                                                        |
|------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|                                    | reproduced below:<br>                                                                                                                 |
| “ethylene oxide (EO) repeat units” | the chemical structure represented by the formula C <sub>2</sub> H <sub>4</sub> O with the following structure reproduced below:<br> |

The parties do not contest these constructions. PO Resp. 25–26; Reply. We determine that no other claim term requires express construction. *See, e.g., Vivid Techs., Inc. v. Am. Sci. & Eng’g, Inc.*, 200 F.3d 795, 803 (Fed. Cir. 1999) (“[O]nly those terms need be construed that are in controversy, and only to the extent necessary to resolve the controversy.”)

#### *B. Asserted Prior Art*

##### *1. Barstad (Ex. 1003)*

Barstad discloses compositions and methods for copper electroplating that are particularly effective in difficult to plate areas having high aspect ratios and small diameter microvias. Ex. 1003, Abs. The processes are applicable to plating a wide variety of articles, including printed circuit boards and other electronic packaging devices. *Id.* at 2:45–48. The compositions disclosed are “particularly useful for filling microvias and trenches required by current and anticipated semiconductor fabrication

requirements (including microvias having aspect ratios of at least 4:1 and diameters of 200 nm or less) by reliably plating copper deposits that are essentially or completely free of voids, inclusions or other plating imperfections.” *Id.* at 2:48–54.

Barstad discloses that the brightener concentration in the preferred electroplating compositions should be maintained and that a “surfactant-type suppressor agent” should be included in the electroplating compositions to achieve bottom-filling deposition. *Id.* at 3:8–25. Specifically, Barstad discloses the following:

In addition to such an elevated brightener concentration, preferably the plating bath also contains a surfactant-type suppressor agent. It has been surprisingly found that use of such a suppressor agent in combination with elevated brightener concentrations can result in effective “bottom-fill” copper plating of a microvia or other aperture without defects such as inclusions or voids. In particular, the suppressor enables enhanced plating rate at the bottom of a microvia, permitting copper to plate the entire aperture space in a substantially “bottom-fill” manner, without premature sealing of the aperture top that can result in inclusions or voids.

*Id.* at 19–30.

Barstad also discloses:

Particularly suitable surfactants for plating compositions of the invention are commercially available polyethylene glycol copolymers, including polyethylene glycol copolymers. Such polymers are available from e.g. BASF (sold by BASF under Tetronic and Pluronic tradenames), and copolymers from Chemax.

*Id.* at 6:51–56.

2. *Morrissey (Ex. 1004)*

Morrissey discloses a process for electroplating copper onto submicron, high-aspect-ratio features of a semiconductor integrated circuit device substrate, while minimizing the concentrations of the organic additives in the plating bath. Ex. 1004 ¶¶ 11, 47. Morrissey seeks to achieve this through use of two different acids in the bath. *Id.* at Abs. Its plating compositions “are particularly useful to plate difficult work pieces, such as circuit board substrates with small diameter, high aspect ratio microvias and other apertures.” *Id.* ¶ 46. Morrissey notes that surfactants may be added to the electroplating baths, with particularly suitable surfactants containing Tetronic polymers. *Id.* ¶ 42.

3. *BASF Catalog (Ex. 1005)*

BASF Catalog is a brochure identifying various Pluronic and Tetronic surfactant products. These surfactant products are block copolymers of ethylene oxide and propylene oxide. Ex. 1005, 3. BASF Catalog notes that “BASF surfactants range from flowable liquids of varying viscosities to pastes, prills, and cast solids, with molecular weights from 1,000 to 30,000.” *Id.* It also describes a spectrum of surfactant products with varying properties: “[t]his brochure covers four block copolymer types—a total of 90 different products—that provide formulating chemists with a broad range of physical properties and surfactant functions to meet targeted performance requirements.” *Id.*

With respect to BASF Catalog, BASF contends that “[t]he last digit of the Tetronic<sup>®</sup> product number, multiplied by 10, is the weight percent of EO in the specific molecule.” Pet. 10 (citing Ex. 1007, 11). BASF’s expert,

Dr. Bruce Pound, calculated the PO:EO ratios for each Tetronic product, with his calculations provided in Table 1 of his declaration. *See* Pet. 10–11. Enthone does not dispute the PO:EO ratios of the Tetronic surfactants as computed by BASF. As such, we accept the calculated the PO:EO ratios for the listed products in BASF Catalog.

*4. Alling (Ex. 1006)*

Alling discloses compositions and methods for electrolytic deposition of metal, such as copper, onto semiconductor wafers. Ex. 1006, Abs. Alling describes a process in which a conductive metal and a more resistive metal may be plated in alternating layers using the same plating bath. *Id.* Alling details that “[p]articularly suitable suppressor agents for plating compositions of the invention are commercially available polyethylene glycol copolymers, including polyethylene glycol copolymers. Such polymers are available from e.g. BASF (sold by BASF under Tetronic® and Pluronic® tradenames).” *Id.* ¶ 43. Alling further states that such suppressor agents are typically added to copper electroplating solutions in a wide range of concentrations between 1 and 10,000 ppm, preferably 5 to 10,000 ppm. *Id.* ¶ 44.

*C. Petitioner’s Contentions*

*1. Obviousness over Barstad, Alling, and BASF Catalog*

BASF asserts that claims 1–6, 8, and 11–18 are unpatentable under 35 U.S.C. § 103 as obvious over the combination of Barstad, Alling, and BASF Catalog. Pet. 4. To support its contentions, and relying on the declaration testimony of Dr. Bruce Pound and Mr. Christopher Utz, BASF

provides analysis purportedly explaining what the combination would have conveyed to one of ordinary skill in the art with respect to the claim limitations and provides reasons why one of ordinary skill in the art would have combined the teachings of the references. Pet. 15–19 (citing Ex. 1002; Ex. 1021). Also, with respect to this ground, BASF provides claim charts and additional discussion of specific elements of the independent and dependent claims. *See id.* at 19–30, 41–57.

In particular, BASF argues that Barstad discloses copper electroplating processes for filling high-aspect ratio, submicron features, such as microvias or trenches, where the solutions employed may contain accelerators and suppressors. Pet. 7–8, 14–15 (citing Ex. 1003, Abs., 2:45–54). BASF argues that, “[t]o achieve the desired bottom-filling deposition, Barstad discloses that one should include a ‘surfactant-type suppressor agent’ in the electroplating compositions.” *Id.* at 8 (citing Ex. 1003, 3:19–21). BASF acknowledges that Barstad does not disclose the use of Tetronic polymers as suppressor agents in its electroplating solution, but argues that Alling provides that Tetronic polymers are particularly suitable as suppressor agents. *Id.* at 9. BASF argues that Tetronic polymers were well-known and that BASF Catalog provides for compounds having PO:EO ratios that fall within the claimed ranges. *Id.* at 15 (citing Ex. 1006 ¶ 43; Ex. 1005, 26).

In combining the references, BASF argues that a person of ordinary skill in the art would have been motivated to use Tetronic polymers as suppressors in Barstad’s compositions and that a person of ordinary skill in the art would have consulted BASF Catalog to identify the available Tetronic polymers. *Id.* at 18–19 (citing Ex. 1002 ¶¶ 20, 28). Specifically, BASF argues as follows:

Prior to the effective filing date of the ‘786 Patent, it was known that small, high-aspect-ratio features, such as trenches and vias, can form undesirable voids during copper electroplating. *See, e.g.*, Barstad, Ex. 1003, 3:25-30. Barstad teaches that “surfactant-type” suppressors reduce void formation. *See id.* 3:20-25. Tetronic<sup>®</sup> polymers are surfactants (Ex. 1005), and Alling teaches that Tetronic<sup>®</sup> polymers are “[p]articularly suitable suppressor agents for plating compositions.” *See* Alling, Ex. 1006, ¶[0043]. Accordingly, a person of ordinary skill in the art would have been motivated to use Tetronic<sup>®</sup> polymers as suppressors in Barstad’s compositions. *See* Pound Decl. ¶28. A person of ordinary skill in the art would have consulted the BASF Catalog to identify the available Tetronic<sup>®</sup> polymers. *See* Utz. Decl., Ex. 1021, ¶¶7-9 (BASF Catalog widely available); Pound Decl. ¶20 (same).

*Id.*

BASF further argues that the genus of Tetronic products is small, that all Tetronic polymers are comprised of propylene oxide and ethylene oxide groups, have the same general chemical structure, and therefore would be expected to behave similarly, and Alling does not identify any Tetronic polymers that would not work as a suppressor in an electrolytic plating composition. *Id.* at 16–17 (citing Ex. 1005, 4, 26; Ex. 1002 ¶¶ 19, 21, 26).

## *2. Obviousness over Morrissey, Alling, and BASF Catalog*

BASF asserts that claims 1–6, 8, and 11–18 are unpatentable under 35 U.S.C. § 103 as obvious over the combination of Morrissey, Alling, and BASF Catalog. Pet. 4. To support its contentions, and relying on the declaration testimony of Dr. Bruce Pound and Mr. Christopher Utz, BASF provides analysis purportedly explaining what the combination would have conveyed to one of ordinary skill in the art with respect to the claim limitations and provides reasons why one of ordinary skill in the art would

have combined the teachings of the references. Pet. 15–19 (citing Ex. 1002; Ex. 1021). Also, with respect to this ground, BASF provides claim charts and additional discussion of specific elements of the independent and dependent claims. *See id.* at 30–57.

In particular, BASF argues that Morrissey discloses copper electroplating processes for filling high-aspect ratio, submicron features, such as microvias or trenches, where the solutions employed may contain accelerators and suppressors, and that both Morrissey and Alling teach that their electroplating compositions may contain Tetronic polymers. Pet. 14–15. BASF also argues that Alling provides that Tetronic polymers are particularly suitable as suppressor agents and that BASF Catalog provides for compounds having PO:EO ratios that fall within the claimed ranges. *Id.* at 15–17. BASF also acknowledges that Morrissey does not disclose the use of Tetronic polymers as suppressor agents in its electroplating solution, but argues that addition of suppressor agents to Morrissey’s composition would have been obvious to a person of ordinary skill in the art in view of Alling and BASF Catalog. *Id.* Specifically, BASF argues as follows:

Morrissey discloses that its electroplating compositions may contain suppressors (*see* Morrissey, Ex. 1004, ¶¶[0039]-[0041]) and that Tetronic<sup>®</sup> polymers may be added to its compositions (*see id.*, ¶[0047]). Because Tetronic<sup>®</sup> polymers are “[p]articularly suitable” suppressors (*see* Alling, Ex. 1006, ¶[0043]), a person of ordinary skill in the art would have been motivated to use Tetronic<sup>®</sup> polymers as suppressor compounds in the compositions of Morrissey. *See* Pound Decl. ¶28. A person of ordinary skill in the art would have consulted the BASF Catalog to identify the available Tetronic<sup>®</sup> polymers. *See* Utz.

Decl., Ex. 1021, ¶¶7-9 (BASF Catalog widely available); Pound Decl. ¶20 (same).

*Id.* at 19.

BASF also argues that the genus of Tetronic products is small, that all Tetronic polymers are comprised of propylene oxide and ethylene oxide groups, and have the same general chemical structure, and therefore would be expected to behave similarly, and Alling does not identify any Tetronic polymers that would not work. *Id.* at 16–17.

BASF also argues that a person of ordinary skill in the art would have been motivated to use Tetronic polymers as suppressors in Morrissey's compositions and that a person of ordinary skill in the art would have consulted BASF Catalog to identify the available Tetronic polymers. Pet. 18–19 (citing Ex. 1002 ¶¶ 20, 28).

#### *D. Discussion*

##### *1. Issues relevant to all challenged claims*

The challenged claims, in their most basic form, recite electrolytic plating compositions containing a source of Cu ions and a suppressor compound. The parties do not dispute that Barstad and Morrissey disclose electrolytic plating compositions containing a source of copper ions. Rather, the parties dispute whether the combination of references suggests electroplating compositions containing a suppressor compound capable of successfully promoting superfilling. *See* PO Resp. 21, 47.

The claims require certain structurally defined suppressor compounds, specifically, suppressor compounds that contain a polyether group comprising a combination of propylene oxide (PO) repeat units and ethylene

oxide (EO) bonded to a nitrogen-containing species. Ex. 1001, 18:19–20:64. The PO:EO ratio and/or molecular weight of the suppressor compounds may vary between specifically defined ranges. *Id.* In this regard, the parties do not dispute that polyethylene glycol copolymers sold under the Tetronic tradename and disclosed in Barstad, Morrissey, Alling, and BASF Catalog fall within the scope of the claims. Pet. 9–11; PO Resp. 35; Ex. 1005; Ex. 1021. Rather, the main thrust of Patent Owner’s argument is that none of the cited references suggests that the known Tetronic compounds would function as suppressors in an electrolytic plating composition for use in a superfilling process.

For example, discussing Barstad and Morrissey, Enthone argues these references disclose compositions that optionally may include a Tetronic compound as a surfactant, not as a suppressor for compositions used in superfilling processes. PO Resp. 36 (citing Ex. 1003, 6:51–58; Ex. 1004 ¶ 42). In particular, Enthone argues that “neither [Barstad nor Morrissey] teaches that a Tetronic surfactant be present in any role in a bath for superfilling rather than conventional plating.” *Id.* (citing Ex. 2031 ¶¶ 92, 94–95, 100).

Discussing Alling, Enthone argues that Alling is different from both Barstad and Morrissey, in that Alling is directed to a conformal plating process, and not a process for superfilling submicron features of a semiconductor substrate. *Id.* at 37–43 (citing Ex. 1006; Ex. 2031 ¶¶ 64, 68–69, 75, 87, 92, 94–104). In particular, Enthone argues as follows:

[T]he plating compositions and processes described in Alling are not compatible with superfilling. Alling lists Tetronic surfactants only as suppressors for conformal plating—a

phenomenon that must be avoided to achieve superfilling, as required by the challenged claims.

*Id.* at 1.

Enthone argues further that the asserted prior art “references of record provide[] no basis for any prediction or reasonable expectation that a cationic surfactant—especially a nitrogenous cationic surfactant having a polyether substituent comprising hydrophobic propylene oxide (PO) repeat units—would possess the critical balance of properties necessary to promote superfilling.” *Id.* at 21 (citing Ex. 2031 ¶ 44); *see also, id.* at 47 (citing Ex. 2031 ¶¶ 81, 86, 87) (“[C]ationic suppressors, or more particularly cationic suppressors comprising alkoxyated amines having hydrophobic PO repeating units, were not contemplated for the more complex and delicate requirements of superfilling.”).

In its Reply, Petitioner argues as follows:

Barstad and Morrissey each independently disclose a superfilling process that includes virtually all of the limitations in the challenged claims. The only limitations even arguably not disclosed in Barstad and Morrissey relate to the specific suppressor component, which includes BASF Tetronic<sup>®</sup> copolymers. Alling clarifies any ambiguity by explicitly stating that Tetronic<sup>®</sup> copolymers are “[p]articularly suitable suppressor agents.” It is undisputed that the BASF Catalog discloses the various physical and chemical properties of Tetronic<sup>®</sup> copolymers claimed in the ‘786 Patent. Given a substantial overlap in the disclosures of Barstad/Morrissey and Alling, a person of ordinary skill using the Barstad/Morrissey process would have followed Alling’s suggestion to use Tetronic<sup>®</sup> copolymers as suppressors.

Reply 1; *see also, id.* at 4 (citing Ex. 1003, 3:19–30, 3:51–55, 6:5–62; Ex. 1004 ¶ 42; Ex. 1005, 028; Ex. 1002 ¶¶ 23–25).

On this record, we are persuaded that Petitioner has shown that the combination of Barstad or Morrissey with Alling would have rendered claims 1–6, 8, and 11–18 obvious. Barstad, Morrissey, and Alling teach or suggest electrolytic plating compositions containing a source of Cu ions and compounds falling within the structural parameters for “suppressor” compounds recited in the claims. Regarding Barstad, Barstad discloses compositions containing a copper salt, an electrolyte, and one or more brightener agents in enhanced concentrations as discussed above, and preferably a suppressor agent. Ex. 1003, 3:41–46. As noted above (Sec. II.B.1), Barstad discloses polyethylene glycol copolymers as preferable “surfactant-type suppressor agents,” and expressly discloses the polyethylene glycol copolymers that were commercially available from BASF under the Tetronic tradename. *Id.* at 6:51–56.

Similarly, Morrissey discloses an electroplating bath containing a source of copper ions, an electrolyte, and additives such as surfactants, brighteners, levelers and suppressants. Ex. 1004 ¶¶ 13–44. Morrissey also expressly discloses polyethylene glycol copolymers, commercially available from BASF under the Tetronic tradename, as suitable surfactants. *Id.* ¶ 42.

Alling also discloses compositions and methods for electrolytic deposition of copper onto semiconductor wafers and expressly discloses that Tetronic copolymers are “[p]articularly suitable suppressor agents for plating compositions.” Ex. 1006, Abs., ¶ 43.

Patent Owner’s various arguments regarding superfilling are not persuasive. The challenged claims do not contain any feature limiting the use of the claimed compositions to superfilling processes. Although we acknowledge the differences between conformal plating and superfilling

submicron features, we are not persuaded that the claims adequately distinguish between compositions useful only for superfilling processes. The broad language of the claims encompasses compositions that may be used in conventional or conformal plating processes and Petitioner has demonstrated by a preponderance of evidence that Alling provides adequate motivation to a person of ordinary skill in the art to use the known Tetronic copolymers as possible suppressor agents in conventional or conformal plating processes as disclosed in Barstad and Morrissey.

At best, the claims' recitation of a "suppressor" merely suggests the "superfilling" function or use of the compounds encompassed by that term. The structure of those compounds are set out positively by the claims. In this regard, there is no dispute that the known Tetronic copolymers satisfy the structural limitations of the claims and necessarily possess the desired characteristics for superfilling processes. Patent Owner's attempt to distinguish the claimed compositions on the basis of a newly discovered function or intended use is not sufficient to establish patentability of those claims. *Application of Loumiet et Lavigne*, 205 F.2d 310, 314 (CCPA 1953) ("That patentability cannot be predicated on a functional or use limitation but must depend upon the recitation of structure that patentably distinguishes over the prior art is a well settled doctrine of Patent Law."); *see also Bettcher Indus., Inc. v. Bunzl USA, Inc.*, 661 F.3d 629, 654 (Fed. Cir. 2011) ("Where all structural elements of a claim exist in a prior art product, and that prior art product is capable of satisfying all functional or intended use limitations, the claimed invention is nothing more than an unpatentable new use for an old product."); *In re Zierden*, 411 F.2d 1325, 1328 (CCPA 1969) ("[M]ere statement of a new use for an otherwise old or obvious

composition cannot render a claim to the composition patentable.”) .

Enthone also argues that, given the distinct difference in function between conventional suppressors and suppressors effective for superfilling, one skilled in the art would have had no reason to substitute a cationic Tetronic surfactant for the exclusively nonionic suppressors taught by Barstad. PO Resp. 46–47. We are not persuaded. Alling, for example, provides sufficient motivation to use a Tetronic copolymer as a suppressor in the conventional or conformal processes of Barstad or Morrissey. Ex. 1006 ¶ 43. The aims of Barstad, Morrissey, and Alling are similar and we are persuaded that Alling would have led one of ordinary skill in the art to use Alling’s suppressor in the conventional or conformal plating solution of Barstad or Morrissey. The aims of eliminating voids and other plating imperfections disclosed in the prior art would have led to obvious variations to meet the goals sought by Barstad and/or Morrissey. Ex. 1003, 2:45–54; Ex. 1004 ¶ 11. As such, we are not persuaded by Enthone’s arguments.

## *2. Issues specific to claims 2, 4, 8, 12–14, and 17*

Specific to claims 2, 4, 8, 12–14, and 17, Enthone argues that these claims narrow the PO:EO ratio to the range of 2:3 to 3:2 and a “very limited minority of the BASF Tetronic compounds have a PO:EO ratio falling within that range.” PO Resp. 60; Ex. 2031, ¶ 105. Enthone further argues as follows:

Nothing in Barstad, Morrissey, or Alling identifies any particular Tetronic compound or suggests any PO:EO range. [Ex. 2031 at ¶105]. Enthone has found that a PO:EO ratio in the claimed

range has a particularly beneficial balance of properties for superfilling. *Id.*

Petitioner responds as follows:

Barstad implies that Tetronic<sup>®</sup> copolymers may be used as **suppressors**. (Ex. 1003 at 3:19–30, 6:5–62). Alling resolves any ambiguity by explicitly stating that “[p]articularly suitable **suppressor** agents” include copolymers “sold by BASF under Tetronic and Pluronic trade-names.” (Ex. 1006 ¶[0043] (emphasis added)). The BASF Catalog describes 22 Tetronic<sup>®</sup> copolymers that were available in 1989. (Ex. 1005 at 028). All have average molecular weights within the claimed range of 1,000–30,000; all but one has a PO:EO ratio of between about 1:9 to about 9:1; and nearly one-third (7 of 22) have a PO:EO ratio in the range of 2:3 to 3:2. (*Id.*; see also Ex. 1002 ¶¶23–25).

Reply 4.

We are persuaded Petitioner sufficiently establishes that a person of ordinary skill in the art was not required to identify the suppressors claimed in the ’786 Patent from an “infinite number” of potential prior art surfactants. BASF Catalog discloses that Tetronic copolymers are a single family of compounds limited to 22 members. Ex. 1005 at 028; Ex. 1028, 197:14–198:1 (“It’s not a very large number.”); Ex. 1029 ¶¶ 41–42.

We are not persuaded that the claims are limited to compositions to be used solely in “superfilling” processes as narrowly defined by Patent Owner. The goal of reliably plating copper deposits that are essentially or completely free of voids, inclusions, or other plating imperfections is explicitly stated in Barstad (Ex. 1003, 2:48–54), such that one of ordinary skill in the art would have been motivated to seek out compounds having the EO:PO ratios and molecular weights that would best serve that goal. BASF Catalog provides compounds that implicitly have those properties, to which

Enthone has acceded, such that providing the ratios and weights identified by Alling, or similar thereto, would have been obvious. This is buttressed by Dr. Pound's testimony that:

In view of the knowledge provided by IBM's achievements and the teachings by Alling, Barstad, and Morrissey, a person of skill in the art would have used Tetronic polymers as suppressor agents in copper electroplating solutions and would have [optimized the] concentration of the suppressors [and other agents] to [] ensure that void formation is avoided.

Ex. 1002 ¶ 29. As such, we do not find Enthone's argument persuasive.

### *3. Issues specific to claim 17*

Specific to claim 17, Enthone argues the following:

Claim 17 specifies a suppressor concentration in the range of 50 to 200 mg/l, i.e., 50–200 ppm. BASF and Dr. Pound (Ex. 1002 at ¶27) note that the 5 to 10,000 ppm suppressor concentration taught by Alling encompasses the 50 to 200 mg/l range called for in claim 17. But the broad genus disclosed by Alling for conformal plating does not suggest the much narrower concentration range tailored to the particular balanced requirements of superfilling. Not only is the concentration range claimed in claim 17 narrower than that disclosed in Alling, but it [also] lies near the extreme end of Alling's broad range. Nothing in Alling provides any motivation to select a suppressor concentration in the range called for by claim 17. Ex. 2031 at ¶ 106.

PO Resp. 60–61. We are not persuaded. The entire concentration range recited in claim 17 is encompassed by the suppressor concentration range disclosed in Alling. Pet. 4. Specifically, Alling discloses the following:

Particularly suitable suppressor agents for plating compositions of the invention are commercially available polyethylene glycol copolymers, including polyethylene glycol

copolymers. Such polymers are available from e.g.,] BASF (sold by BASF under Tetronic and Pluronic tradenames) . . . .

Such suppressor agents are typically added to copper electroplating solutions in concentrations ranging from about 1 to 10,000 ppm based on the weight of the bath, more preferably about 5 to 10,000 ppm.

Ex. 1006 ¶¶ 43–44. When the above disclosure is combined with, for example, Barstad’s teaching that “surfactant-type” suppressors reduce void formation (Ex. 1003, 3:20–25), we are persuaded that a person of ordinary skill in the art would have been motivated to arrive at a concentration within the claimed range by optimizing the concentration of suppressors and other agents to reduce void formation. Pet. 18–19, Ex. 1003, 2:45–54; Ex. 1004 ¶ 11; Ex. 1002 ¶ 29; *In re Peterson*, 315 F.3d 1325, 1330 (Fed. Cir. 2003) (“[W]hen, as here, the claimed ranges are completely encompassed by the prior art, the conclusion is even more compelling than in cases of mere overlap. The normal desire of scientists or artisans to improve upon what is already generally known provides the motivation to determine where in a disclosed set of percentage ranges is the optimum combination of percentages.”); *see also, In re Boesch*, 617 F.2d 272, 276 (CCPA 1980) (“[D]iscovery of an optimum value of a result effective variable in a known process is ordinarily within the skill of the art.” (citations omitted)).

Enthone’s contention that the recited concentration ranges would only have been sufficient for superfilling processes is not supported by sufficient evidence. For example, there is insufficient evidence on this record demonstrating that the claimed range is critical or achieves unexpected results relative to the range disclosed by Alling. Accordingly, we are not persuaded by Enthone’s arguments in this regard.

#### 4. *Alleged secondary considerations*

As to secondary considerations, we note that factual inquiries for an obviousness determination include secondary considerations based on evaluation and crediting of objective evidence of nonobviousness. *Graham v. John Deere Co.*, 383 U.S. 1, 17 (1966). Notwithstanding what the teachings of the prior art would have suggested to one with ordinary skill in the art at the time of the invention, the totality of the evidence submitted, including objective evidence of nonobviousness, may lead to a conclusion that the claimed invention would not have been obvious to one with ordinary skill in the art. *In re Piasecki*, 745 F.2d 1468, 1471–1472 (Fed. Cir. 1984).

However, such a conclusion requires the finding of a nexus to establish that the evidence relied upon traces its basis to a novel element in the claim and not to something in the prior art. *Institut Pasteur & Universite Pierre et Marie Curie v. Focarino*, 738 F.3d 1337, 1347 (Fed. Cir. 2013). All types of objective evidence of nonobviousness must be shown to have nexus. *In re GPAC Inc.*, 57 F.3d 1573, 1580 (Fed. Cir. 1995) (nexus generally); *In re Huang*, 100 F.3d 135, 140 (Fed. Cir. 1996) (commercial success); *Rambus Inc. v. Rea*, 731 F.3d 1248, 1256 (Fed. Cir. 2013) (long-felt need); *Muniauction, Inc. v. Thomson Corp.*, 532 F.3d 1318, 1328 (Fed. Cir. 2008) (praise); *Stamps.com Inc. v. Endicia, Inc.*, 437 F. App'x 897, 905 (Fed. Cir. 2011) (unpublished) (skepticism).

Patent Owner argues that several lines of objective evidence (or “secondary considerations”) demonstrate the non-obviousness of the challenged claims. PO Resp. 57–59. In particular, Patent Owner argues long-felt but unmet need, skepticism, praise, and failure of others. *Id.*

Patent Owner's arguments with regard to each of the secondary considerations, however, fail to establish a nexus between the invention disclosed and claimed in the '786 patent and any asserted objective evidence of non-obviousness. Rather, the discussion of secondary considerations relates to the merits of processes for superfilling submicron features of a semiconductor substrate. As discussed above, however, the challenged claims encompass obvious compositions for use in known processes of conventional and conformal plating and capable of use in processes for superfilling submicron features of a semiconductor substrate. Accordingly, the objective evidence does not weigh in favor of a conclusion that claim 1–6, 8, and 11–18 are non-obvious.

### III. CONCLUSION

Having considered the parties' arguments and evidence, we evaluate all of the evidence together to make a final determination of obviousness. *In re Cyclobenzaprine Hydrochloride Extended-Release Capsule Patent Litig.*, 676 F.3d 1063, 1075 (Fed. Cir. 2012) (stating that a fact finder must consider all evidence relating to obviousness before finding patent claims invalid). In so doing, we conclude that Petitioner has satisfied its burden of demonstrating, by a preponderance of the evidence, that the subject matter of claims 1–6, 8, and 11–18 of the '786 patent would have been obvious over (1) the combination of Barstad, Alling, and BASF Catalog and (2) the combination of Morrissey, Alling, and BASF Catalog.

IV. ORDER

In consideration of the foregoing, it is hereby:

ORDERED that claims 1–6, 8, and 11–18 of the '786 Patent are held unpatentable; and

FURTHER ORDERED that this is a Final Written Decision; therefore, parties to the proceeding seeking judicial review of the decision must comply with the notice and service requirements of 37 C.F.R. § 90.2.

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