



(51) International Patent Classification:

C07C 69/40 (2006.01) C08F 2/22 (2006.01)
C07C 69/704 (2006.01) C08K 5/10 (2006.01)
C07C 59/265 (2006.01) C10M 145/06 (2006.01)
C07C 55/10 (2006.01) C10M 145/16 (2006.01)

(21) International Application Number:

PCT/US2016/069107

(22) International Filing Date:

29 December 2016 (29.12.2016)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

15203160.5 30 December 2015 (30.12.2015) EP

(71) Applicant: AFTON CHEMICAL CORPORATION
[US/US]; 500 Spring Street, Richmond, VA 23219 (US).(72) Inventors: ROSS, Matthew, Paul; 2 Barn Grove, Auden-
shaw, Manchester M34 5GA (GB). WILLIAMS, Carl; 12
Sophia Way, Bradwell, Newcastele Under Lyme, Stafford-
shire ST5 8TB (GB). ANDERSON, Steven; 5 The Coach
House, Lawton Hall Drive, Church Lawton, Cheshire ST7
3BG (GB). JARVIS, Anthony, Nicholas; 8 Parkfield
Road, Spital, Wirral CH63 3DS (GB).(74) Agent: CHEN, Tani; Wolf, Greenfield & Sacks, P.C., 600
Atlantic Avenue, Boston, MA 02210-2206 (US).(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,
AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,
BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM,
DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,
HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KH, KN,
KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA,
MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG,
NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS,
RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY,
TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN,
ZA, ZM, ZW.(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,
GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ,
TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU,
TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE,
DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU,
LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK,
SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,
GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

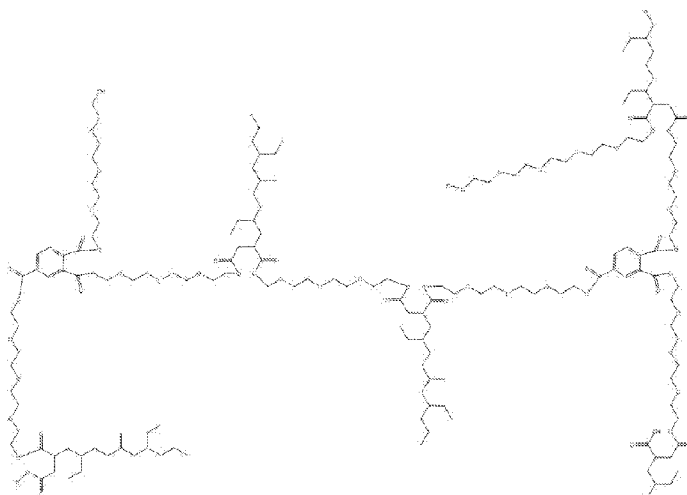
(54) Title: POLYMERIC EMULSIFIER AND LUBRICITY ADDITIVES FOR AQUEOUS METAL REMOVAL FORMING
ROLLING, OR OTHER APPLICATIONS

FIG. 1

(57) **Abstract:** The present invention generally relates to fluids for metalworking and other applications and, in particular, to compounds useful in such fluids. For instance, some aspects of the invention are generally directed to molecular compounds comprising polydentate acids (and derivatives thereof), polyalkylene glycols, and anhydrides (e.g., alkyl and/or alkenyl succinic anhydrides, and/or derivatives thereof), which may be reacted together, e.g., covalently, to form a compound useful for such fluids. An example of a polydentate acid is trimellitic acid; an example of a polyalkylene glycol is polyethylene glycol; an example of an anhydride is poly(isobutenylsuccinic anhydride). Such compounds can be used, for example, for emulsification and/or lubrication purposes, and/or as corrosion inhibiting agents. Such compounds can also be used in some cases to control foaming, and/or provide stability to hard water, for example, when included into a metalworking fluid formulation. Other embodiments are generally directed to fluids containing such compounds, which may be used for metalworking or other applications, methods for making or using such compounds, kits including such compounds, or the like.



**POLYMERIC EMULSIFIER AND LUBRICITY ADDITIVES FOR AQUEOUS
METAL REMOVAL, FORMING, ROLLING, OR OTHER APPLICATIONS**

FIELD

5 The present invention generally relates to fluids for metalworking and other applications and, in particular, to additives useful in such fluids.

BACKGROUND

10 Metalworking operations include rolling, forging, hot-pressing, blanking, bending, grinding, stamping, drawing, cutting, turning, milling, punching, spinning and the like. Such operations generally use a metalworking fluid to provide lubrication, cooling and removal of swarf, which can reduce the power required, prevent sticking, or decrease wear of the materials and tools that are used. Metalworking fluids may comprise a variety of fluids, including straight oils, or water based such as soluble or emulsions, semi-synthetic fluids, and synthetic fluids. However, traditional emulsifiers used in most metalworking applications
15 were not designed for metalworking use, and accordingly suffer from a number of defects. For instance, emulsifiers tolerant of hard water tend to produce excessive foam in soft water. In contrast, soft water low foam emulsifiers tend to produce deposits or scum, leading to depletion in hard waters. Emulsifiers such as amides and sulfonates are highly susceptible to bacterial degradation in use, leading to shortened fluid life and a heavy reliance on toxic
20 substances such as biocides to inhibit degradation. Accordingly, improvements in emulsifiers for metalworking applications are needed.

SUMMARY

25 The present invention generally relates to fluids for metalworking and other applications and, in particular, to additives useful in such fluids. The subject matter of the present invention involves, in some cases, interrelated products, alternative solutions to a particular problem, and/or a plurality of different uses of one or more systems and/or articles.

30 In one aspect, the present invention is generally directed to a molecular compound comprising at least a first portion derived from a polydentate acid or a polydentate acid derivative, a second portion derived from polyalkylene glycol, and a third portion derived from an anhydride or derivative thereof. In some cases, the first portion is covalently bonded to the second portion, and the second portion is covalently bonded to the third portion.

 In another set of embodiments, the composition comprises a compound formed by a method comprising covalently bonding a polydentate acid and/or polydentate acid derivative,

a polyalkylene glycol and/or an ethoxylated alcohol, and an anhydride and/or an anhydride derivative to form the compound

In yet another set of embodiments, the composition comprises a compound formed by a method comprising covalently bonding a polydentate acid, a polyalkylene glycol and/or an ethoxylated alcohol, and a succinic anhydride to form the compound.

In some embodiments, the compositions discussed herein, including the above compositions, can be used to stabilize hard water, or control foam formation, e.g., by reducing the amount of foaming that occurs, for example, when included into a metalworking fluid formulation.

The present invention, in another aspect, is generally directed to a method. According to one set of embodiments the method is a method for producing a composition, e.g., any of the compositions described herein. In another set of embodiments, the method comprises reacting a polydentate acid and/or polydentate acid derivative, an anhydride and/or an anhydride derivative, and a polyalkylene glycol and/or an ethoxylated alcohol to produce a product. The method, in yet another set of embodiments, comprises reacting a polydentate acid and/or anhydride, a succinic anhydride, and a polyalkylene glycol and/or an ethoxylated alcohol to produce a product.

In still another aspect, the present invention is generally directed to a method of using a composition, e.g., any of the compositions described herein. For example, certain embodiments are generally directed to methods of using compositions such as those described herein for metalworking and other applications, for additives for use in compositions suitable for metalworking and other applications, for use as emulsifiers, for use as lubricants, e.g., metal lubricants, etc. In another set of embodiments, the compositions discussed herein, including the above compositions, are used to stabilize hard water, or control foam formation, e.g., by reducing the amount of foaming that occurs. Other examples of suitable uses include any of those described herein.

In yet another aspect, the present invention is generally directed to a lubricant comprising a molecular compound comprising at least, a first portion derived from a polydentate acid or a polydentate acid derivative, a second portion derived from polyalkylene glycol, and a third portion derived from an anhydride or derivative thereof. In some cases, the first portion is covalently bonded to the second portion, and the second portion is covalently bonded to the third portion. In some cases, the present invention is generally directed to method of using the lubricant, e.g., for lubrication purposes.

The present invention, in still another aspect, is generally directed to a lubricant comprising a molecular compound comprising at least, a first portion derived from a polydentate acid or a polydentate acid derivative, a second portion derived from polyalkylene glycol, and a third portion derived from an anhydride or derivative thereof. In some cases, the first portion is covalently bonded to the second portion, and the second portion is covalently bonded to the third portion. In some embodiments, the present invention is generally directed to method of using the emulsion.

Following are sentences describing additional embodiments of the invention.

1. A composition, comprising a molecular compound comprising at least: (a) a first portion derived from one or more polydentate acids or a polydentate acid derivatives that are capable of forming at least three ester groups; (b) a second portion derived from one or more polyalkylene glycols; and (c) a third portion derived from one or more anhydrides or derivatives thereof, wherein the one or more anhydrides or derivatives thereof are other than polydentate acids or polydentate acid derivatives that are capable of forming at least three ester groups; and wherein the first portion is covalently bonded to the second portion, and the second portion is covalently bonded to the third portion.

2. The composition of sentence 1, wherein the first portion is derived from at least one or more of trimellitic acid, trimellitic anhydride, citric acid, and citric anhydride.

3. The composition of any preceding sentence, wherein the second portion is derived from one or more polyethylene glycols.

4. The composition of any preceding sentence, wherein the second portion is derived from at least one difunctional polyalkylene glycol, preferably at least two difunctional polyalkylene glycols.

5. The composition of any preceding sentence, wherein the second portion is derived from at least one monofunctional polyalkylene glycol.

6. The composition of any preceding sentence, wherein the molecular compound further comprises a portion derived from a non-alkoxylated alcohol, preferably wherein the non-alkoxylated alcohol is monofunctional or polyfunctional.

7. The composition of any preceding sentence, wherein the third portion is derived from at least one of succinic anhydride, alkyl succinic anhydride, and alkenyl succinic anhydride.

8. The composition of any preceding sentence, wherein the third portion is derived from at least one PIBSA, preferably at least two PIBSAs, preferably wherein the at least two PIBSA components are of different molecular weight.

9. The composition of any preceding sentence, wherein the third portion is derived from at least one alkyl or alkenyl succinic anhydride other than PIBSA.

10. The composition of any preceding sentence, wherein the second portion is derived from at least two difunctional polyalkylene glycol components and at least one
5 monofunctional polyalkylene glycol, and wherein the at least two difunctional polyalkylene glycol derivatives are of different molecular weight or are different polyalkylene glycols.

11. The composition of any preceding sentence, wherein the overall mole ratio of the third portion to the first portion is between 1:1 and 10:1, preferably between 4:1 and 8:1; and/or wherein the overall mole ratio of the second portion to the third portion is between
10 0.5:1 and 10:1, preferably between 1:1 and 5:1; and/or wherein the overall mole ratio of the second portion to the first portion is between 1:1 and 15:1, preferably between 6:1 and 14:1.

12. A composition, comprising: a molecular compound comprising at least: (a) a first portion derived from a polydentate acid or a polydentate acid derivative, wherein the polydentate acid comprises three or more -COOH moieties; (b) a second portion derived
15 from polyalkylene glycol; and (c) a third portion derived from an anhydride or derivative thereof; wherein the first portion is covalently bonded to the second portion, and the second portion is covalently bonded to the third portion.

13. The composition of sentence 12, wherein at least one first portion is derived from one or more of trimellitic acid, trimellitic anhydride, citric acid, or citric anhydride;
20 and/or wherein at least one second portion is derived from polyethylene glycol; and/or wherein at least one third portion is derived from succinic anhydride, alkyl succinic anhydride, and/or alkenyl succinic anhydride.

14. The composition of any one of sentences 12 or 13, wherein the composition comprises more than one first portion, more than one second portion, and/or more than one
25 third portion.

15. The composition of any preceding sentence, wherein the compound has an M_w of at least 1000 daltons, preferably between 1000 and 100,000 daltons, more preferably between 2000 and 20,000 daltons, even more preferably between 3000 and 5000 daltons, or between 5000 and 15,000 daltons or between 5000 and 50,000 daltons.

30 16. The composition of any preceding sentence, wherein the composition complies with one or more of the following (i) or (ii): (i) wherein the compound has an HLB of less than 18, wherein the compound has an HLB of between 2 and 16, or wherein the compound has an HLB of less than 14, preferably wherein the compound has an HLB of less than 12, preferably wherein the HLB is determined by Griffin's method; and/or (ii) wherein

the compound has an acid value of between 2 mg KOH/g and 40 mg KOH/g, preferably between 5 mg KOH/g and 20 mg KOH/g, more preferably between 6 mg and 16 mg KOH/g, or wherein the compound has an acid value of between 1 mg KOH/g and 20 mg KOH/g, preferably between 2 mg and 12 mg KOH/g, preferably wherein the acid value is determined via ASTM D974.

17. The composition of any preceding sentence, wherein the composition is a metalworking fluid, optionally further comprising at least water and/or an oil, preferably wherein the metalworking fluid is a semi-synthetic metalworking fluid.

18. A method of producing a composition according to any preceding sentence, the method comprising: reacting (i) a polydentate acid and/or polydentate acid derivative, (ii) an anhydride and/or an anhydride derivative, and (iii) a polyalkylene glycol and/or an ethoxylated alcohol to produce a product, wherein the polydentate acid and/or polydentate acid derivative is capable of forming at least three ester groups.

19. The method of sentence 18, wherein the method comprises: reacting the anhydride and/or an anhydride derivative, and the polyalkylene glycol and/or the ethoxylated alcohol to produce an intermediate; and reacting the intermediate with the polydentate acid and/or the polydentate acid derivative to produce the product, wherein the polydentate acid and/or polydentate acid derivative is selected from the group consisting of trimellitic acid, trimellitic anhydride and citric acid, and wherein the anhydride is derived from succinic anhydride, alkenyl succinic anhydride, and/or alkyl succinic anhydride.

20. The method of sentence 18 or 19, wherein the polydentate acid and/or the polydentate acid derivative and the polyalkylene glycol and/or the ethoxylated alcohol react via an esterification reaction.

21. The method of any one of sentences 18-20, comprising heating the reaction mixture to at least 160 °C, preferably to at least 180 °C, and/or to no more than 230 °C.

22. The method of any one of sentences 18-21, wherein the composition complies with one or more of the following (i) – (ii): (i) comprising reacting until the product has an acid value of at least 4 mg KOH/g, preferably until the product has an acid value of at least 12 mg KOH/g; and/or (ii) wherein the reacting occurs under vacuum or under nitrogen.

23. A composition, comprising: a compound formed by a method comprising covalently bonding a polydentate acid and/or polydentate acid derivative, a polyalkylene glycol and/or an ethoxylated alcohol, and an anhydride and/or an anhydride derivative to form the compound, preferably via an esterification reaction, optionally wherein the method is the method according to any one of sentences 18-22.

24. A composition, comprising a molecular compound comprising at least: (a) a first portion derived from a polydentate acid or a polydentate acid derivative; (b) a second portion derived from polyalkylene glycol; and (c) a third portion derived from an anhydride or derivative thereof; wherein the first portion is covalently bonded to the second portion, and the second portion is covalently bonded to the third portion.

25. The composition of sentence 24, wherein at least one first portion is derived from trimellitic acid.

26. The composition of any one of sentences 24 or 25, wherein at least one first portion comprises a polydentate acid or polydentate acid derivative having three or more –COOH moieties.

27. The composition of any one of sentences 24-26, wherein at least one first portion is derived from trimellitic anhydride.

28. The composition of any one of sentences 24-27, wherein at least one first portion is derived from citric acid.

29. The composition of any one of sentences 24-28, wherein at least one second portion is derived from polyethylene glycol.

30. The composition of any one of sentences 24-29, wherein at least one second portion has a formula $-(CH_2-CH_2-O)_n-$, wherein n is less than or equal to 250.

31. The composition of any one of sentences 24-30, wherein at least one second portion has a formula $-(CH_2-CH_2-O)_n-$, wherein n is less than or equal to 50.

32. The composition of any one of sentences 24-31, wherein at least one second portion has a formula $-(CH_2-CH_2-O)_n-$, wherein n is inclusively between 1 and 10.

33. The composition of any one of sentences 24-32, wherein at least one second portion has an M_w of less than about 20,000 daltons.

34. The composition of any one of sentences 24-33, wherein at least one second portion has an M_w of less than about 10,000 daltons.

35. The composition of any one of sentences 24-34, wherein at least one second portion has an M_w of less than about 1,000 daltons.

36. The composition of any one of sentences 24-35, wherein at least one second portion has an M_w of less than about 750 daltons.

37. The composition of any one of sentences 24-36, wherein at least one second portion has an M_w of less than about 400 daltons.

38. The composition of any one of sentences 24-37, wherein at least one second portion has an M_w of less than about 250 daltons.

39. The composition of any one of sentences 24-38, wherein at least one second portion comprises an alkyl chain of length C_1 to C_{20} .

40. The composition of any one of sentences 24-39, wherein at least one second portion comprises an alkyl chain of length C_{10} to C_{18} .

5 41. The composition of any one of sentences 24-40, wherein at least one third portion is derived from succinic anhydride.

42. The composition of any one of sentences 24-41, wherein at least one third portion is derived from alkyl succinic anhydride.

10 43. The composition of any one of sentences 24-42, wherein at least one third portion is derived from alkenyl succinic anhydride.

44. The composition of any one of sentences 24-43, wherein at least one third portion is derived from poly(isobutenylsuccinic anhydride).

45. The composition of any one of sentences 24-44, wherein at least one third portion has an M_w of between about 100 daltons and about 20,000 daltons.

15 46. The composition of any one of sentences 24-45, wherein at least one third portion has an M_w of between about 200 daltons and about 600 daltons.

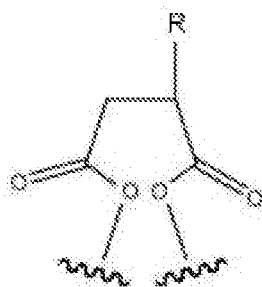
47. The composition of any one of sentences 24-46, wherein at least one third portion has an M_w of between about 200 daltons and about 4,000 daltons.

20 48. The composition of any one of sentences 24-47, wherein at least one third portion has an M_w of between about 300 daltons and about 1,000 daltons.

49. The composition of any one of sentences 24-48, wherein at least one third portion has an M_w of less than about 500 daltons.

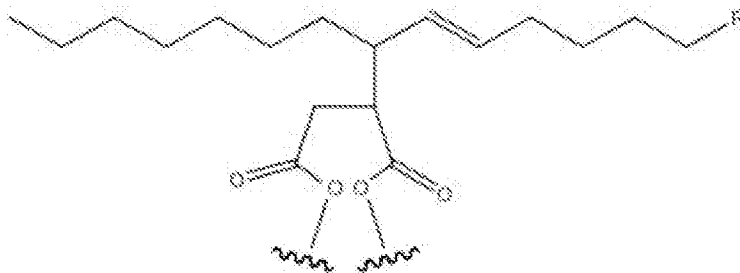
50. The composition of any one of sentences 24-49, wherein at least one third portion has an M_w of between about 300 daltons and about 400 daltons.

25 51. The composition of any one of sentences 24-50, wherein at least one third portion has a structure:



wherein R is an alkyl or an alkenyl group.

52. The composition of any one of sentences 24-51, wherein at least one third portion has a structure:



wherein R is an n-alkyl group having between 1 and 6 carbon atoms, inclusively.

5 53. The composition of any one of sentences 24-52, wherein the composition comprises more than one first portion.

54. The composition of sentence 53, wherein at least two of the first portions are identical.

10 55. The composition of any one of sentences 24-54, wherein the composition comprises more than one second portion.

56. The composition of sentence 55, wherein at least two of the second portions are identical.

57. The composition of any one of sentences 24-56, wherein the composition comprises more than one third portion.

15 58. The composition of sentence 57, wherein at least two of the third portions are identical.

59. The composition of any one of sentences 24-58, wherein the overall mole ratio of the third portion to the first portion is between 1:1 and 10:1.

20 60. The composition of any one of sentences 24-59, wherein the overall mole ratio of the third portion to the first portion is between 4:1 and about 8:1.

61. The composition of any one of sentences 24-60, wherein the overall mole ratio of the second portion to the third portion is between about 0.5:1 and about 10:1.

62. The composition of any one of sentences 24-61, wherein the overall mole ratio of the second portion to the third portion is between about 1:1 and about 5:1.

25 63. The composition of any one of sentences 24-62, wherein the overall mole ratio of the second portion to the first portion is between about 1:1 to about 15:1.

64. The composition of any one of sentences 24-63, wherein the overall mole ratio of the second portion to the first portion is between about 6:1 to about 14:1.

65. The composition of any one of sentences 24-64, wherein the compound has an M_w of at least about 1000 daltons.

66. The composition of any one of sentences 24-65, wherein the compound has an M_w of between about 1000 and about 100,000 daltons.

5 67. The composition of any one of sentences 24-66, wherein the compound has an M_w of between about 2000 and about 20,000 daltons.

68. The composition of any one of sentences 24-67, wherein the compound has an M_w of between about 3000 and about 5000 daltons.

10 69. The composition of any one of sentences 24-68, wherein the compound has an M_w of between about 5000 and about 15,000 daltons.

70. The composition of any one of sentences 24-69, wherein the compound has an M_w of between about 5000 and about 50,000 daltons.

71. The composition of any one of sentences 24-70, wherein the compound has an HLB of less than about 18.

15 72. The composition of sentence 71, wherein the HLB is determined by Griffin's method.

73. The composition of any one of sentences 24-72, wherein the compound has an HLB of between about 2 and about 16.

20 74. The composition of any one of sentences 24-73, wherein the compound has an HLB of less than about 14.

75. The composition of any one of sentences 24-74, wherein the compound has an HLB of less than about 12.

76. The composition of any one of sentences 24-75, wherein the compound has an acid value of between about 2 mg KOH/g and about 40 mg KOH/g.

25 77. The composition of any one of sentences 24-76, wherein the compound has an acid value of between about 1 mg KOH/g and about 20 mg KOH/g.

78. The composition of any one of sentences 24-77, wherein the compound has an acid value of between about 5 mg KOH/g and about 20 mg KOH/g.

30 79. The composition of any one of sentences 24-78, wherein the compound has an acid value of between about 6 mg KOH/g and about 16 mg KOH/g.

80. The composition of any one of sentences 24-79, wherein the compound has an acid value of between about 2 mg KOH/g and about 12 mg KOH/g.

81. The composition of any one of sentences 76-80, wherein the acid value is determined via ASTM D974.

82. The composition of any one of sentences 24-81, wherein the composition is a metalworking fluid.

83. The composition of sentence 82, wherein the metalworking fluid is a semi-synthetic metalworking fluid.

5 84. The composition of any one of sentences 24-83, wherein the composition further comprises water.

85. The composition of any one of sentences 24-84, wherein the composition further comprises an oil.

10 86. The composition of any one of sentences 24-85, wherein the composition is a random polymer.

87. The composition of any one of sentences 24-85, wherein the composition is not a random polymer.

15 88. A method, comprising reacting a polydentate acid and/or polydentate acid derivative, an anhydride and/or an anhydride derivative, and a polyalkylene glycol and/or an ethoxylated alcohol to produce a product.

89. The method of sentence 88, wherein the method comprises reacting the anhydride and/or an anhydride derivative, and the polyalkylene glycol and/or the ethoxylated alcohol to produce an intermediate; and reacting the intermediate with the polydentate acid and/or the polydentate acid derivative to produce the product.

20 90. The method of any one of sentences 88 or 89, wherein the polydentate acid and/or the polydentate acid derivative and the polyalkylene glycol and/or the ethoxylated alcohol react via an esterification reaction.

91. The method of any one of sentences 88-90, comprising heating the reaction mixture to at least about 160 °C.

25 92. The method of any one of sentences 88-91, comprising heating the reaction mixture to at least about 188 °C.

93. The method of any one of sentences 88-92, comprising heating the reaction mixture to no more than 230 °C.

30 94. The method of any one of sentences 88-93, comprising reacting until the product has an acid value of at least about 4 mg KOH/g.

95. The method of any one of sentences 88-94, comprising reacting until the product has an acid value of at least about 9 mg KOH/g.

96. The method of any one of sentences 88-95, wherein the reacting occurs under vacuum.

97. The method of any one of sentences 88-96, wherein the reacting occurs under nitrogen.

98. The method of any one of sentences 88-97, wherein the polydentate acid or polydentate acid derivative has three or more –COOH moieties.

5 99. A composition, comprising a compound formed by a method comprising covalently bonding a polydentate acid and/or polydentate acid derivative, a polyalkylene glycol and/or an ethoxylated alcohol, and an anhydride and/or an anhydride derivative to form the compound, preferably via an esterification reaction, optionally wherein the method is the method according to any one of sentences 88-98.

10 100. A composition, comprising a compound formed by a method comprising covalently bonding a polydentate acid and/or polydentate acid derivative, a polyalkylene glycol and/or an ethoxylated alcohol, and an anhydride and/or an anhydride derivative to form the compound.

15 101. The composition of sentence 100, wherein the polydentate acid and/or polydentate acid derivative, and the polyalkylene glycol and/or the ethoxylated alcohol react via an esterification reaction.

102. The composition of any one of sentences 100 or 101, wherein the method comprises heating the reaction mixture to at least about 160 °C.

20 103. The composition of any one of sentences 100-102, wherein the method comprises heating the reaction mixture to at least about 188 °C.

104. The composition of any one of sentences 100-103, wherein the method comprises reacting until the product has an acid value of at least about 4 mg KOH/g.

105. The composition of any one of sentences 100-104, wherein the method comprises reacting until the product has an acid value of at least about 10 mg KOH/g.

25 106. The composition of any one of sentences 100-105, wherein the polydentate acid or polydentate acid derivative has three or more –COOH moieties.

In another aspect, the present invention encompasses methods of making one or more of the embodiments described herein, for example, additives for metalworking fluids and other applications. In still another aspect, the present invention encompasses methods of
30 using one or more of the embodiments described herein, for example, additives for metalworking fluids and other applications.

Other advantages and novel features of the present invention will become apparent from the following detailed description of various non-limiting embodiments of the invention when considered in conjunction with the accompanying figures. In cases where the present

specification and a document incorporated by reference include conflicting and/or inconsistent disclosure, the present specification shall control. If two or more documents incorporated by reference include conflicting and/or inconsistent disclosure with respect to each other, then the document having the later effective date shall control.

BRIEF DESCRIPTION OF THE DRAWINGS

Non-limiting embodiments of the present invention will be described by way of example with reference to the accompanying figures, which are schematic and are not intended to be drawn to scale. In the figures, each identical or nearly identical component illustrated is typically represented by a single numeral. For purposes of clarity, not every component is labeled in every figure, nor is every component of each embodiment of the invention shown where illustration is not necessary to allow those of ordinary skill in the art to understand the invention. In the figures:

Fig. 1 illustrates a compound in accordance with one embodiment of the invention;

Fig. 2 illustrates a compound in accordance with another embodiment of the invention;

Fig. 3 illustrates trimellitic anhydride;

Figs. 4A-4B illustrate certain polyalkylene glycol structures;

Fig. 5 illustrates a reactant comprising a 5-member succinic anhydride ring; and

Figs. 6A-6C illustrate certain compounds for use within certain embodiments of the invention.

DETAILED DESCRIPTION

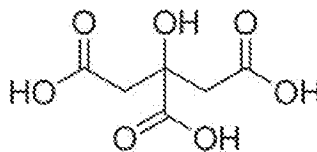
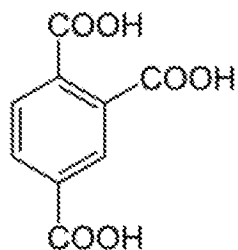
The present invention generally relates to fluids for metalworking and other applications and, in particular, to compounds useful in such fluids. For instance, some aspects of the invention are generally directed to molecular compounds comprising polydentate acids (and derivatives thereof), polyalkylene glycols, and anhydrides (e.g., alkyl and/or alkenyl succinic anhydrides, and/or derivatives thereof), which may be reacted together, e.g., covalently, to form a compound useful for such fluids. An example of a polydentate acid is trimellitic acid; an example of a polyalkylene glycol is polyethylene glycol; an example of an anhydride is poly(isobutenylsuccinic anhydride). Such compounds can be used, for example, for emulsification and/or lubrication purposes, and/or as corrosion inhibiting agents. Such compounds can also be used in some cases to control foaming, and/or provide stability to hard water, for example, when included into a metalworking fluid formulation. Other embodiments are generally directed to fluids containing such compounds,

which may be used for metalworking or other applications, methods for making or using such compounds, kits including such compounds, or the like.

In one aspect, the present invention is generally directed to compositions comprising polydentate acid portions (or derivatives thereof), polyalkylene glycol portions, and anhydride portions (or derivatives thereof), which may be covalently bonded together to form compounds in various arrangements. For example, a compound may have one or more polydentate acid portions (or derivatives thereof), one or more of polyalkylene glycol portions, and one or more anhydride portions (or derivatives thereof). Optionally, other portions may be present as well.

In some cases, the composition may include one or more portions derived from polydentate acids and/or polydentate acid derivatives. Examples of polydentate acids include, but are not limited to: diacids, such as saturated alkane dioic acids including: oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, brassilic acid, dodecanedioic acid, thapsic acid; unsaturated dioic acids such as: maleic acid, fumaric acid, glutaconic acid, traumatic acid, muconic acid, glutinic acid, citraconic acid, mesaconic acid, itaconic acid; aromatic dicarboxylic acids such as: phthalic acid, isophthalic acid, terephthalic acid, diphenic acid, substituted dioic acids such as: aspartic acid, malic acid, glutamic acid, diaminopimelic acid, tartronic acid, tartaric acid, arabinaric acid, saccharic acid, mesoxalic acid, oxaloacetic acid, acetonedicarboxylic acid; aliphatic or other tricarboxylic acids such as: citric acid, isocitric acid, aconitic acid, propane-1,2,3-tricarboxylic acid, 1,2,4-butanetricarboxylic acid; aromatic tricarboxylic acids such as: trimesic acid, trimellitic acid, hemimellitic acid; tetra acids such as: ethylenediaminetetraacetic acid, 1,2,3,4-butanetetracarboxylic acid, 1,2,4,5-benzenetetracarboxylic acid, furantetracarboxylic acid, 1,2,3,4-cyclobutanetetracarboxylic acid; other polydentate acids include mellitic acid, and derivatives of any of these. It should be understood that the term "aromatic" also encompasses heterocyclic versions thereof. Also included as examples of polydentate acid derivatives are any acid anhydride, halogenated acid COX where X is F, Cl, Br or I, and esters and the like, including but not limited to any of those polydentate acids described above, e.g., as is shown in Fig. 3. Thus, in one embodiment, the composition includes a portion derived from a polydentate and/or a polydentate acid derivative, such as citric acid or trimellitic acid. In some cases, the composition may include more than one such portion, and the portions may be the same or different. For instance, each such portion may be independently derived from one or more polydentate acids and/or one or more polydentate acid derivatives.

A polydentate acid may have two, three, or more -COOH moieties that can react in various ways. In some cases, the polydentate acid has three or more -COOH moieties. For example, the structures of trimellitic acid and citric acid are respectively as follows:



5 In addition, in some embodiments, more than one polydentate acid portion may be present in a compound. In such cases, the polydentate acid portions may independently be the same or different. See Fig. 1 for a non-limiting example of a structure containing trimellitic acid portions.

10 Without wishing to be bound by any theory, it is believed that such polydentate acid functionality may provide a macro-structural component, for example, by providing multiple reaction locations via the various -COOH moieties. Such functionality may be important, for instance, for emulsion stability, emulsion particle size, etc., by facilitating a macromolecular structure that, for example, enhances film formation or emulsion stabilization.

15 In addition, in some embodiments, the compound can also comprise non-alkoxylated alcohols. The non-alkoxylated alcohols can be, for instance, monofunctional (comprising just one OH group), or polyfunctional (comprising at least two OH groups). Monofunctional alcohols are generally given by the structure R-OH . R may be, e.g., a straight or branched alkyl chain or aromatic group. Examples include saturated and unsaturated C_1 to C_{22} alcohols, or aromatic alcohols such as benzyl alcohol, phenol and derivatives thereof. The R group can also comprise other functional groups known in organic chemistry. The monofunctional alcohols can be, for example, primary, secondary, or tertiary alcohols.

20 Similarly, polyfunctional alcohols include di-ols and other poly-ols. Examples of di-ols include those represented by the general formula $\text{HO-C}_n\text{H}_{2n}\text{-OH}$, where n is any integer from 2 to 100. Other example di-ols include those where at least one or both OH groups are not located in a chain terminal position such as 1,3-butanediol, or 2,4-hexanediol. Other example polyols include tri-ols such as glycerol, or tetra-ols such as pentaerythritol. Other polyols include polyhydroxy phenols, and sugars and carbohydrates. However, it should be understood that in still other embodiments, the compound is free of non-alkoxylated alcohols, such as monofunctional and/or polyfunctional alcohols.

The compound may also contain one or more portions derived from polyalkylene glycols. In some cases, the composition may include more than one such polyalkylene glycol portion, and the portions may be the same or different. These may be covalently bound to the polydentate acid portions (or derivative thereof), for instance, through esterification reactions where an –OH moiety on the polyalkylene glycol reacts with a –COOH moiety to produce water and an ester bond. Such portions may arise from, for example, polyethylene glycol and/or ethoxylated alcohols that may be present. In some embodiments, the polyalkylene glycol portions may be useful for controlling the hydrophilic-lipophilic balance of the compound, e.g., as discussed below.

Non-limiting examples of polyalkylene glycols include polyethylene glycols. The polyethylene glycol portions may include any suitable number of ethylene glycol repeat units (i.e., –CH₂–CH₂–O– repeat units). See, e.g., Fig. 6A. In some cases, there may be less than 1,000, less than 500, less than 250, less than 100, less than 50, or less than 25 ethylene glycol repeat units. In some embodiments, for example, a polyethylene glycol portion may contain 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, or more repeat units.

The polyalkylene glycol portions may also have any suitable molecular weights (M_w), for example, less than about 500,000 daltons, less than about 100,000 daltons, less than about 50,000 daltons, less than about 20,000 daltons, less than about 10,000 daltons, less than about 5,000 daltons, less than about 1,000 daltons, less than about 750 daltons, less than about 500 daltons, less than about 400 daltons, less than about 300 daltons, etc.

The polyalkylene glycol portions may be unsymmetrical in some embodiments with an alkyl chain present at one end of the molecule and a hydroxyl group at the other. The alkyl chain can be of any length and may be saturated or unsaturated, e.g., C₁ to C₂₈, for instance, C₁₀ to C₁₈. For example, the alkyl chain may be C₁, C₂, C₃, C₄, C₅, C₆, C₇, C₈, C₉, C₁₀, C₁₁, C₁₂, C₁₃, C₁₄, C₁₅, C₁₆, C₁₇, C₁₈, C₁₉, C₂₀, C₂₁, C₂₂, C₂₃, C₂₄, C₂₅, C₂₆, C₂₇, C₂₈, C₂₉, C₃₀, etc. Specific non-limiting examples of unsymmetrical polyalkylene glycols include, but are not limited to, alkoxylated non-ionic surfactants such as ethoxylated, propoxylated or butoxylated non-ionic surfactants, and co-polymers thereof such as EO/PO, EO/BO and PO/BO non-ionic surfactants (EO = ethylene oxide; PO = propylene oxide; BO = butylene oxide). Additional examples of non-ionic surfactants include, but are not limited to, the Brij range supplied by Croda, the Emulsogen range supplied by Clariant, the Tergitol and Ecosurf range, supplied by Dow. However, these are not necessarily present in all embodiments, and thus may be absent in some cases. The alkyl chain can be straight-chained or branched, and may in some cases contain other function groups. The polyalkylene glycol portions can also

be terminated with carboxylic acid or thiol groups in some cases, e.g., rather than hydroxyl groups. See, e.g., Figs. 4A and 4B for non-limiting examples of polyalkylene glycol portions having an alkyl chain present at one end. These figures illustrate compounds that are naturally sourced (e.g., as the Z-isomer), and in some cases are acquired as a mixture of C₁₆ and C₁₈ structures.

In addition, as discussed, more than one polyethylene glycol portion may be present in a compound; if so, the polyethylene glycol portions may each independently have the same or different numbers of repeat units. A non-limiting example of a structure containing polyethylene glycol portions can be seen in Fig. 1. Several different polyethylene glycol portions are present in this example. Other suitable polyalkylene glycols include: polypropylene glycol, polybutylene glycols both straight chain and branched, poly-THF (tetrahydrofuran), copolymers of different alkylene glycol monomers such as EO-PO (ethylene oxide-propylene oxide) copolymers, oil soluble PAGs (polyalkylene glycols) or OSPs (oil soluble polyalkylene glycols) such as PO-BO copolymers (propylene oxide-butylene oxide), poly alpha olefins, polystyrene oxides, and other polyether type compounds. Where the polyalkylene glycol is a co-polymer it can be, for example, block, random, or a reverse block co-polymer.

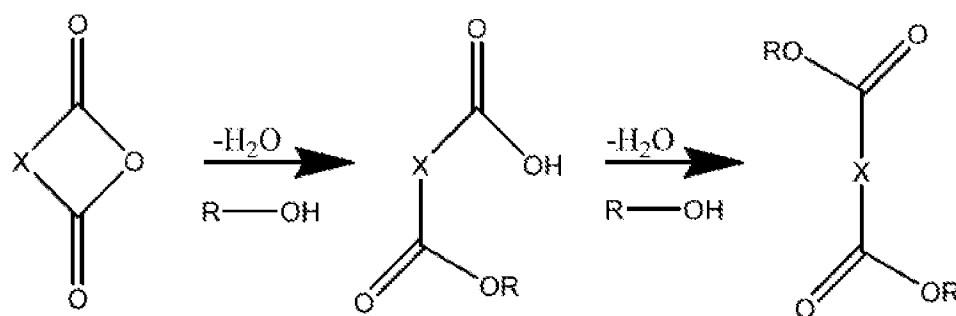
The compound may also contain one or more portions derived from anhydrides and/or derivatives thereof, e.g., covalently bonded to the polydentate acid portions (or derivative thereof) and/or the polyalkylene glycol portions. In some cases, more than one such anhydride portion may be present within a compound, and such portions may independently be the same or different. For example, each such portion may be independently derived from one or more anhydrides and/or one or more anhydride derivatives.

According to some embodiments of the present invention, the third portion or the third portions, i.e. the one or more third portion(s), may each be independently derived from substituted or unsubstituted succinic anhydride and derivatives. In addition, in some cases, the third portion is different from the first portion in the molecular compound or is derived from a compound other than the first portion, or the third portion may not be derived from a polydentate acid or polydentate acid derivative, for example, containing three or more – COOH moieties that can react in various ways, or are capable of forming at least three ester groups.

As well as anhydrides, such as substituted or unsubstituted succinic anhydrides, the parent carboxylic acids, such as substituted or unsubstituted succinic acids, and other derivatives thereof can also be used in certain embodiments, such as substituted or

unsubstituted succinic esters and/or substituted or unsubstituted succinic acid halides. In some embodiments, the anhydride may be the initial form of the anhydride portion, prior to its incorporation into a compound, i.e., the anhydride may link to the compound via ester groups formed by the anhydride compound reacting with alcohol groups (R-OH), e.g., as

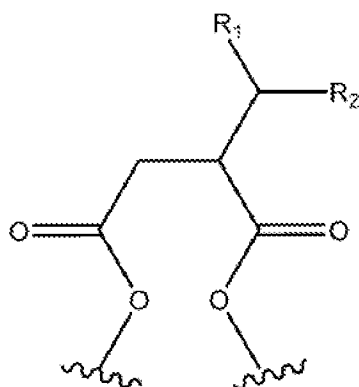
5 follows:



In some cases, the composition may include one or more alkyl succinic anhydride portion(s) and/or one or more alkenyl succinic anhydride portion(s) and/or one or more alkyl succinic acid portion(s) and/or one or more alkenyl succinic acid portion(s) and/or one or more alkyl succinic ester portion(s) and/or one or more alkenyl succinic ester portion(s) and/or one or more alkyl succinic acid halide portion(s) and/or one or more alkenyl succinic acid halide portion(s). One non-limiting example of an alkenyl succinic anhydrides is poly(isobutenylsuccinic anhydride) ("PIBSA"). See, e.g., Fig. 6B for non-limiting examples of PIBSA. Other non-limiting examples include alkenyl succinic anhydrides that react with

10

15 alcohols to form the following moiety:

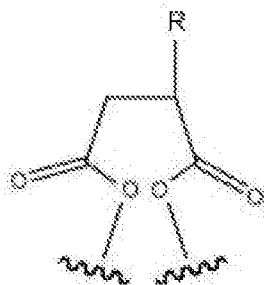


where the wavy lines indicate covalent bonding to other portions of the compound, e.g., to polydentate acid portions (or derivatives thereof) and/or polyalkylene glycol portions. R₁ may be an H or an alkyl, e.g., containing between 1 and 20 carbon atoms, and may be linear (i.e., an n-alkyl) or branched, and/or may contain unsaturated groups such as C=C; it may

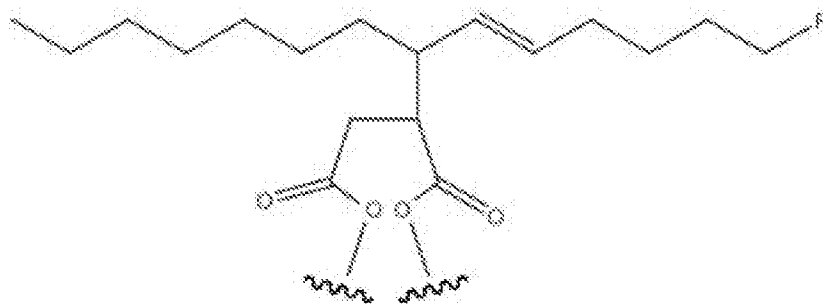
20 also be substituted or unsubstituted. R₂ may be an alkyl, e.g., containing between 1 and 20

carbon atoms, and may be linear (i.e., an n-alkyl) or branched or may contain unsaturated groups such as C=C, and it may be substituted or unsubstituted.

One non-limiting example of an anhydride is:



- 5 where the wavy lines indicate covalent bonding to other portions of the compound, e.g., to polydentate acid portions (or derivatives thereof) and/or polyalkyl glycol portions, such as those discussed herein. R may be an alkyl or an alkenyl group (e.g., containing 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, or more carbon atoms), and R may be linear or branched, and/or substituted or unsubstituted. As a non-limiting example, R may be a polyisobutenyl group, including any of those described herein. A specific non-limiting example of an anhydride is:



- 15 where R in this structure may be a C₁ to C₆ alkyl chain, e.g., containing 1, 2, 3, 4, 5, or 6 carbon atoms, and may be linear (i.e., an n-alkyl) or branched. R may also be substituted or unsubstituted. Other examples include branched forms of the alkyl chains within the above structure. Non-limiting examples of commercially available alkenylsuccinic anhydrides include the products Pentasize 8 and Pentasize 68 (ex. Pentagon) wherein the alkenyl groups are unsaturated C₁₈ units (Pentasize 8) or a mixture of C₁₆/C₁₈ units (Pentasize 68).

- 20 It should be noted that upon reaction, the 5-member ring of the succinic anhydride portion opens and reacts with other portions (e.g., to polyalkylene glycol) within the compound, as indicated in the structure above with the wavy lines. Non-limiting examples of such ring-opened alkenyl succinic anhydride portion are shown in Figs. 1 and 2; see also Figs. 5 and 6C.

Such anhydride portions (or derivatives thereof) may be useful, for example, to inhibit degradation, e.g., via bacterial attack, or to control foaming without scum formation, e.g., in applications involving soft water or hard water. Thus, in one set of embodiments, any of the compounds as discussed herein can be used to stabilize hard water, or control foam formation, e.g., by reducing the amount of foaming that occurs. See, e.g., Example 4, discussed below.

The anhydride portion (or derivative thereof) may have any suitable molecular weight. In some embodiments, the anhydride portion may have a molecular weight less than about 20,000 daltons, less than 3,000 daltons, e.g., between about 100 daltons and about 5,000 daltons, between about 100 daltons and about 20,000 daltons, between about 200 daltons and about 4,000 daltons, between about 200 daltons and about 1,000 daltons, or between about 300 daltons and about 1,000 daltons, between about 300 daltons to about 600 daltons, or between about 400 daltons and about 500 daltons. In some cases, the molecular weight may be controlled by R groups or repeat units within the portion (e.g., the number of repeat units of isobutylene in PIBSA). Non-limiting examples of PIBSAs are shown in Fig. 6B. In addition, in some cases, more than one anhydride portion (or derivative thereof) may be present within a compound, and such portions may independently be the same or different, and each portion may independently be, for example, derived from an anhydride portion or an anhydride derivative, etc. In addition, in some cases, the compound may include imide versions of the anhydride compounds thereof, e.g. succinimides, e.g., in addition and/or instead of any of the anhydride portions described herein. Many of these anhydrides and anhydride derivatives can be readily obtained commercially.

It should be noted that the polydentate acid portions, polyalkylene glycol portions, and anhydride portions may be covalently bonded directly together, or indirectly through one or more linkers, to form the compound. In some cases, for example, the polydentate acid portions may be covalently bonded to the polyalkylene glycol portions and/or the anhydride portions. Likewise, in some cases, the anhydride portions may be covalently bonded to the polydentate acid portions and/or the polyalkylene glycol portions. In some cases, the polyalkylene glycol portions may be covalently bonded to the polydentate acid portions and/or the anhydride portions. In addition, it should be noted that not all of these bonding arrangements need be present in the compound.

As mentioned, in some embodiments, there may be more than one polydentate acid portion (or derivative thereof), and/or more than one polyalkylene glycol portion, and/or more than one anhydride portion present in the compound. Thus, for example, the compound

may have a molecular weight of at least about 1000 daltons. For example, the molecular weight may be between about 1000 and about 200,000 daltons, between about 1000 and about 100,000 daltons, between about 1100 and about 100,000 daltons, between about 1200 and about 10,000 daltons, between about 2000 and about 20,000 daltons, or between about 2000 and about 10,000 daltons. As additional examples, the compound has a molecular weight of about 3000 to 5000 daltons, e.g., about 4000 daltons, about 5,000 to about 10,000 daltons, or about 5,000 to about 15,000 daltons, about 5,000 to about 25,000 daltons, or about 5,000 to about 50,000 daltons. In some cases, the compound may have a weight average molecular weight suitable for emulsification (for instance, between about 3,000 to about 5,000 daltons, or any other suitable molecular weights described herein). In certain embodiments, the compound may have a weight average molecular weight suitable for lubricity (for example, between about 5,000 daltons to about 50,000 daltons, or any other suitable molecular weights described herein). In addition, in some embodiments, the polymers may be suitable for use as corrosion inhibiting agents.

Within such compounds, the portions derived from polydentate acids and/or derivatives thereof, the portions derived from polyalkylene glycols, and the portions derived from anhydrides and/or derivatives thereof may be present at any suitable molar ratio. For example, the ratio of the polydentate acid portions to the alkyl and/or alkenyl succinic anhydride portions may be between 1:0.1 and 1:1, for instance, between 1:0.2 and 1:0.9, or 1:0.4 and about 1:0.8. As another non-limiting example, the molar ratio of the alkyl and/or alkenyl succinic anhydride portions to the ethylene glycol portions may be between about 0.1:1 and about 0.5:1, or between about 0.2:1 and about 0.3:1. In yet another example, the overall mole ratio of the polydentate acid portion to the polyalkylene glycol portion may be between about 1:1 to about 1:4, for instance, between about 1:2 to about 1:3.

In another set of embodiments, the ratio of the alkyl and/or alkenyl succinic anhydride portions to the polydentate acid portions (e.g., the third portion to the first portion) may be between 1:1 and 10:1, for instance, between 4:1 and 8:1, between 3:1 and 10:1, between 5:1 and 10:1, between 1.5:1 and 6:1, between 1.5:1 and 7:1, or between 6:1 and 8:1. As another non-limiting example, the molar ratio of the ethylene glycol portions to the alkyl and/or alkenyl succinic anhydride portions (e.g., the second portion to the third portion) may be between 0.5:1 and 10:1, for example, between 1:1 and 5:1, between 1.4:1 and 3:1, between 1:1 and 5:1, between 1:1 and 3:1, or between 1:1 and 2:1. In yet another example, the overall mole ratio of the polyalkylene glycol portion to the polydentate acid portion (e.g., the second portion to the first portion) may be between 1:1 and 15:1, for instance, between 6:1 and 14:1,

between about 2:1 to about 3:1, between about 1.2:1 and 10:1, between 1:1 and 10:1, between 1:1 and 15:1, between 5:1 and 15:1, between 1:1 and 11:1, between 8:1 and 12:1, or between 9:1 and 11:1.

In some embodiments, the polymers can also comprise other functional groups.

- 5 These functional groups can be based on, for example, nitrogen such as amino groups, sulfur such as sulfide or sulfate groups, halogens such as chlorine, or phosphorous such as phosphate ester groups. In other embodiments, however, the polymer may not comprise such functional groups.

- 10 In addition, in some cases, a range of compounds such as these may be present within a mixture, which may have the same or different structures. In some cases, the above numbers are determined as averages (e.g., weight averaged) of the compounds present within the mixture.

- Some aspects of the invention are also generally directed to techniques and methods for making any of the compounds discussed herein. For example, in one set of embodiments, 15 the invention is generally directed to reacting a polydentate acid and/or anhydride, a succinic anhydride, and a polyalkylene glycol and/or an ethoxylated alcohol to produce a compound, e.g., as discussed herein. Such reactions may include esterification reactions. In some cases, the succinic anhydride and the polyalkylene glycol and/or the ethoxylated alcohol may first be reacted to produce an intermediate, then the intermediate with the polydentate acid, 20 although in other cases, a compound may be prepared by adding some or all of the reactants to a suitable reaction vessel and heating the reactants together for a suitable length of time to produce the compounds. For instance, reactants may be mixed together and heated until the compounds have a desired acid value, e.g., any of the acid values described herein. In some cases, the compound may be a polymer, such as a block, random, or a reverse block co- 25 polymer. For instance, the polymer may be a random polymer, e.g., formed by reacting the polydentate acid and/or anhydride, succinic anhydride, and polyalkylene glycol and/or ethoxylated alcohol together simultaneously. In other embodiments, however, any two of these may first be reacted, followed by the third. Thus, in some embodiments, the polymer is not a random polymer.

- 30 A suitable catalyst can also be optionally used to help expedite the reaction. Non-limiting examples of such suitable catalysts are p-toluene sulphonic acid or methane sulphonic acid. The reaction mixture may also optionally include a small quantity of a substance added to control the color of the reaction mixture. Suitable compounds include anti-oxidants or oxygen scavengers. Non-limiting examples of suitable anti-oxidants include

phosphites, specific examples of which include triisodecyl phosphite, butylated hydroxytoluene, and the like.

In some cases, a reaction mixture may be heated to a temperature of at least about 100 °C, at least about 120 °C, at least about 150 °C, at least about 160 °C, at least about 170 °C, at least about 180 °C, at least about 190 °C, at least about 200 °C, or any other suitable temperature. In some cases, the temperature may be no more than about 250 °C, no more than about 240 °C, no more than about 230 °C, no more than about 220 °C, no more than about 210 °C, or no more than about 200 °C. In some cases, the reaction may be performed under partial vacuum (e.g., less than 700 mmHg, less than 500 mmHg, or less than 300 mmHg), or under enriched nitrogen (e.g., at least about 80%, at least about 85%, at least about 90%, or at least about 95% nitrogen, on a volumetric basis).

Such compounds may be used, in certain aspects, as surfactants, emulsifiers, or lubricants. For instance, the compounds can be used to emulsify any suitable “oil in water” or “water in oil” system, or indeed any two or more suitable immiscible phases. Non-limiting examples of oils that the compounds discussed herein can be emulsified with include: Group I, II, III, IV and V base oils including: mineral oils, such as paraffinic and naphthenic oils, vegetable oils, synthetic oils such polyalphaolefins, and esters such as TMPTO.

The compounds can be used in various embodiments in any product that requires emulsification. Non-limiting examples include products for use in greases, engine oils, fuels, hydraulic fluids, driveline fluids, automatic and manual transmission fluids, mining and drilling fluids, slideway fluids, turbine fluids, motion compensators, drilling fluids (e.g., for offshore oil drilling applications or the like), and gear fluids. Any engine or motor oil may be used in various embodiments. Other examples include personal and household care products, cleaning products, products for use in textile and leather processing, surface coatings including paints and printing inks.

In some cases, the hydrophilic-lipophilic balance (HLB) may be controlled, for example, by controlling the polyalkylene glycol portions within the compound, e.g., to produce desired effects. By varying the ratio of hydrophobic to hydrophilic monomers, the HLB value of the compounds described herein can tailored for the specific system it will be applied to. The hydrophilic-lipophilic balance of a compound is generally a measure of the degree to which it is hydrophilic or lipophilic. Techniques for determining HLB are known to those of ordinary skill in the art, and include Griffin’s method (see, e.g., Griffin, “Classification of Surface-Active Agents by ‘HLB,’” *J. Soc. Cosmetic Chem.*, 1(5):311-326, 1949, or “Emulsions,” W.C. Griffin, in the Kirk-Othmer Encyclopedia of Chemical

Technology, 3rd Edition, 8, 900-930 (1979)). In various embodiments, the HLB of the compound (or average HLB of a mixture) may be less than about 18, less than about 16, less than about 14, less than about 12, less than about 8, less than about 5, or less than about 3. In some cases, for example, the HLB may be between about 8 and about 16, or between about 2 and about 16, e.g., about 11.

In addition, in some cases, the compound may have an acid value of between about 1 mg KOH/g to about 40 mg KOH/g. For example, the acid value may be about 1 mg KOH/g and about 20 mg KOH/g, or between about 2 mg KOH/g and about 40 mg KOH/g. In some cases, the acid value may be at least about 3 mg KOH/g, at least about 4 mg KOH/g, at least about 5 mg KOH/g, at least about 6 mg KOH/g, at least about 8 mg KOH/g, at least about 10 mg KOH/g, at least about 12 mg KOH/g, etc. For example, the compound may have an acid value of between about 2 mg KOH/g and about 12 mg KOH/g, between about 5 mg KOH/g and about 20 mg KOH/g, between about 8 mg KOH/g and about 12 mg KOH/g, between about 6 mg KOH/g and about 16 mg KOH/g, or between about 2 mg and about 8 mg KOH/g. In some cases, lower acid values (e.g., between about 2 mg KOH/g and about 10 mg KOH/g, or other acid values described herein) may be useful for lubrication. In certain embodiments, somewhat higher acid values (e.g., between about 7 mg KOH/g and about 15 mg KOH/g, or other acid values described herein) may be useful for emulsification. Generally, the acid value is a measure of the acidity of a compound, and is the mass of potassium hydroxide (KOH) in milligrams that is required to neutralize one gram of the compound. Those of ordinary skill in the art will be aware of techniques for determining acid values, e.g., by using ASTM D974. In some cases, acid values are reported without units, i.e., the “mg KOH/g” is implicitly present.

As mentioned, compounds such as those discussed herein may be used in a wide variety of applications. For example, the compounds may be used as surfactants, emulsifiers, corrosion inhibitors, or lubricants. As a non-limiting example, in one set of embodiments, a compound as discussed herein may be used within a metalworking fluid, e.g., for various metalworking applications such as deforming and removal processes such as rolling, forging, hot-pressing, blanking, bending, stamping, drawing, cutting, milling, grinding, turning, punching, spinning and the like. Metal working fluids comprising compounds such as those disclosed herein can be, for example, fully synthetic, semi-synthetic, milky oil in water emulsions, or neat oils. Metal working fluids comprising compounds such as those disclosed herein can be finished fluids/concentrates or packages. In some embodiments, the

metalworking fluid may include a lubricating oil and one or more compounds such as those disclosed herein, which may be used as additives within the lubricating oil.

Examples of lubricating oils include, but are not limited to, natural and/or synthetic oils. Examples of lubricating oils include liquid petroleum oils and solvent-treated or acid-treated mineral lubricating oils of the paraffinic, naphthenic and mixed paraffinic-naphthenic types. Additional examples of oils include hydrocarbon oils and halo-substituted hydrocarbon oils such as polymerized and interpolymers of olefins (e.g., polybutylenes, polypropylenes, propylene-isobutylene copolymers, chlorinated polybutylenes, poly(1-hexenes), poly(1-octenes), poly(1-decenes), etc.); alkylbenzenes (e.g., dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di(2-ethylhexyl)benzenes); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenyls), etc. Other examples include dicarboxylic acid esters (e.g., phthalic acid, succinic acid, alkyl succinic acids and alkyl and/or alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkyl malonic acids, alkenyl malonic acids) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether, propylene glycol); also ricinoleic acid and self-polymerized versions thereof. Still other examples include silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy-, or polyaryloxysiloxane oils and silicate oils, such as tetraethyl silicate, tetraisopropyl silicate, tetra-(2-ethylhexyl) silicate, tetra-(4-methyl-2-ethylhexyl) silicate, tetra-(p-tert-butylphenyl) silicate, hexa-(4-methyl-2-pentoxo)disiloxane, poly(methyl)siloxanes and poly(methylphenyl)siloxanes.

A variety of other additives may be present within the metalworking fluid. Non-limiting examples include: coupling agents, antiwear additives, extreme pressure additives such as phosphorous compounds such as phosphate esters and sulfur compounds such as polysulfides, antioxidants, pH buffers, oil (e.g., naphthenic or paraffinic oils), water (e.g., tap water, distilled water, deionized water, treated water, etc.), biocides (e.g., bacteriocides or fungicides) including both formaldehyde releasing and formaldehyde free biocides, foam inhibitors, rust inhibitors, lubricating agents such as ricinoleic acid or self-polymerized versions thereof, corrosion inhibitors, polymers, or the like. Many of these are commercially available.

Non-limiting examples of corrosion inhibitors include alkali and alkanolamine salts of carboxylic acids, undecandioic/dodecandioic acid and its salts, C₄₋₂₂ carboxylic acids and their salts, boric acids, compounds and their salts, tolyltriazole and its salts, benzotriazoles and its salts, imidazolines and its salts, alkanolamines and amides, sulfonates, alkali and

alkanolamine salts of naphthenic acids, phosphate ester amine salts, alkali nitrites, alkali carbonates, carboxylic acid derivatives, alkylsulfonamide carboxylic acids, arylsulfonamide carboxylic acids, fatty sarkosides, phenoxy derivatives and sodium molybdate. Other non-limiting examples include: tertiary polyamines such as pentamethyl dipropyl-triamine and salts thereof, such as alkyl polyalkylene glycol ether phosphate salts, as taught in EP2930229 (A1). Other examples includes products to passivate or prevent staining of metals such as aluminium, copper and other yellow metals such as brass. Many of these are commercially available.

Non-limiting examples of alkalinity agents to control the pH include alkanolamines (primary, secondary and tertiary), aminomethylpropanol (AMP-95), diglycolamine (DGA), monoethanolamine (MEA), monoisopropanolamine (MIPA), butylethanolamine (NBEA), dicyclohexylamine (DCHA), diethanolamine (DEA), butyldiethanolamine (NBDEA), triethanolamine (TEA), metal alkali hydroxides, potassium hydroxide, sodium hydroxide, magnesium hydroxide, lithium hydroxide, metal carbonates and bicarbonates, sodium carbonate, sodium bicarbonate, potassium carbonate and potassium bicarbonate.

The compounds disclosed herein may also be used in other types of emulsified oil systems besides metalworking fluids. For example, the compounds may be used in oil field chemicals such as drilling fluids and cementing chemicals, paper chemicals (i.e., chemicals used in the manufacture of paper), explosive emulsions, rock drill lubricants, mining lubricants, or the like.

For example, in one set of embodiments, the compound disclosed herein may be used in a base oil. The base oil used in the compositions herein may be selected from any suitable base oil. Examples include the base oils in Groups I-V as specified in the American Petroleum Institute (API) Base Oil Interchangeability Guidelines. These five base oil groups are as follows:

TABLE 4

Base oil Category	Sulfur (%)		Saturates (%)	Viscosity Index
Group I	> 0.03	and/or	<90	80 to 120
Group II	≤0.03	and	≥90	80 to 120
Group III	≤0.03	and	≥90	≥120
Group IV	All			

	polyalphaolefins (PAOs)			
Group V	All others not included in Groups I, II, III, or IV			

Groups I, II, and III are mineral oil process stocks. Group IV base oils contain true synthetic molecular species, which are produced by polymerization of olefinically unsaturated hydrocarbons. Many Group V base oils are also true synthetic products and may include diesters, polyol esters, polyalkylene glycols, alkylated aromatics, polyphosphate esters, polyvinyl ethers, and/or polyphenyl ethers, and the like, but may also be naturally occurring oils, such as vegetable oils. It should be noted that although Group III base oils are derived from mineral oil, the rigorous processing that these fluids undergo causes their physical properties to be very similar to some true synthetics, such as PAOs. Therefore, oils derived from Group III base oils may be referred to as synthetic fluids in the industry.

The base oil used in the composition described herein may be a mineral oil, animal oil, vegetable oil, synthetic oil, or mixtures thereof. Suitable oils may be derived from hydrocracking, hydrogenation, hydrofinishing, unrefined, refined, and re-refined oils, and mixtures thereof.

Unrefined oils are those derived from a natural, mineral, or synthetic source without or with little further purification treatment. Refined oils are similar to the unrefined oils except that they have been treated in one or more purification steps, which may result in the improvement of one or more properties. Examples of suitable purification techniques are solvent extraction, secondary distillation, acid or base extraction, filtration, percolation, and the like. Oils refined to the quality of an edible may or may not be useful. Edible oils may also be called white oils. In some embodiments, the compositions are free of edible or white oils.

Re-refined oils are also known as reclaimed or reprocessed oils. These oils are obtained similarly to refined oils using the same or similar processes. Often these oils are additionally processed by techniques directed to removal of spent additives and oil breakdown products.

Mineral oils may include oils obtained by drilling or from plants and animals or any mixtures thereof. For example such oils may include, but are not limited to, castor oil, lard oil, olive oil, peanut oil, corn oil, soybean oil, rapeseed oil and linseed oil, as well as mineral lubricating oils, such as liquid petroleum oils and solvent-treated or acid-treated mineral lubricating oils of the paraffinic, naphthenic or mixed paraffinic-naphthenic types. Such oils may be partially or fully hydrogenated, if desired. Oils derived from coal or shale may also be useful.

Useful synthetic lubricating oils may include hydrocarbon oils such as polymerized, oligomerized, or interpolymerized olefins (e.g., polybutylenes, polypropylenes, propyleneisobutylene copolymers); poly(1-hexenes), poly(1-octenes), trimers or oligomers of 1-decene, e.g., poly(1-decenes), such materials being often referred to as alpha-olefins, and mixtures thereof; alkyl-benzenes (e.g. dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di-(2-ethylhexyl)-benzenes); polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenyls); diphenyl alkanes, alkylated diphenyl alkanes, alkylated diphenyl ethers and alkylated diphenyl sulfides and the derivatives, analogs and homologs thereof or mixtures thereof. Polyalphaolefins are typically hydrogenated materials.

Other synthetic lubricating oils include polyol esters, diesters, liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, and the diethyl ester of decane phosphonic acid), or polymeric tetrahydrofurans. Synthetic oils may be produced by Fischer-Tropsch reactions and typically may be hydroisomerized Fischer-Tropsch hydrocarbons or waxes. In one embodiment oils may be prepared by a Fischer-Tropsch gas-to-liquid synthetic procedure as well as other gas-to-liquid oils.

The major amount of base oil included in a composition described herein may be selected from the group consisting of Group I, Group II, a Group III, a Group IV, a Group V, and a combination of two or more of the foregoing, and wherein the major amount of base oil is other than base oils that arise from provision of additive components or viscosity index improvers in the composition. In another embodiment, the major amount of base oil included in a composition described herein may be selected from the group consisting of Group II, a Group III, a Group IV, a Group V, and a combination of two or more of the foregoing, and wherein the major amount of base oil is other than base oils that arise from provision of additive components or viscosity index improvers in the composition.

The amount of the oil present may be the balance remaining after subtracting from 100 wt% the sum of the amount of the performance additives inclusive of viscosity index improver(s) and/or pour point depressant(s) and/or other top treat additives. For example, the

oil that may be present in a finished fluid may be a “major amount,” such as greater than about 50 wt%, greater than about 60 wt%, greater than about 70 wt%, greater than about 80 wt%, greater than about 85 wt%, greater than about 90 wt%, or greater than 95 wt%.

Unless clearly indicated to the contrary, molecular weights as used herein are weight average molecular weights (abbreviated herein as M_w).

As used herein in the specification and in the claims, the term “aromatic” refers to an organic compound containing a planar unsaturated ring of atoms that is stabilized by an interaction of the bonds forming the rings. The term “aliphatic” refers to an organic compound containing atoms forming an open chain or a non-aromatic ring. An aromatic or aliphatic compound may contain only carbon atoms or may contain one or more heteroatoms.

The following examples are intended to illustrate certain embodiments of the present invention, but do not exemplify the full scope of the invention.

EXAMPLE 1

This example is generally directed to polymeric additives that are designed for aqueous metalworking applications, such as metal removal, forming or rolling. The additives in this example are emulsifiers with lubricity attributes or lubricity with co-emulsification attributes determined by molecular weight/reagent charge ratio/acid value. Some embodiments are directed to a low foaming hard water tolerant long life emulsifier for metal removal applications. An example of such a compound is shown in Fig. 1. This polymeric additive can be used in place of most existing metal working emulsifiers at lower overall treatment rate and with improved overall performance.

The polymeric additives in this example are built by the reaction of components selected to provide functionalities desirable for metalworking applications. Branched components, such as PIBSAs (poly(isobutenylsuccinic anhydride)s), were selected to contribute low foam and foam control or air release in both soft water and hard water without scum formation. Branched components were selected to inhibit degradation by bacterial attack.

Hydrophilic components, such as polyethylene glycols, were selected to modify HLB (the Hydrophilic-Lipophilic Balance) in conjunction with the PIBSA moieties. By selection of polyethylene glycols and the charge ratio with the PIBSAs, the HLB could be varied from low HLB (desirable for lubricity) to medium HLB (desirable for emulsification) and any combinations in between.

The addition of a polydentate acid functionality, such as trimellitic acid (and/or anhydride), citric acid or similar provides a macro-structural component. This may be important to the long life emulsion stability, emulsion particle size, etc., by facilitating a macromolecular structure that enhances film formation and emulsion stabilization.

5 The molecular weight can be controlled by controlling the both charge ratio of the components and the acid value. The polymer may be produced via esterification reactions with the acid value falling as both acid and hydroxyl moieties are consumed in the esterification process. Molecular weights from 1000 to greater than 100,000 daltons could be produced, as determined by the application requirements. For example good emulsification
10 has been demonstrated for polymers between 2000 and 10,000 daltons.

A weight average molecular weight of between about 3000 and 5,000 Daltons may be used for polymers used primarily for emulsification and between 5,000 and about 10,000 Daltons may be used for polymers used primarily for lubrication. Although it should be understood that polymers with weight average molecular weight of between 3000 and about
15 5,000 Daltons may offer lubrication benefits and those between about 5,000 and about 10,000 Daltons may offer emulsification benefits.

EXAMPLE 2

A polymeric emulsifier was prepared as follows. The following reagents were added to a stirred, temperature controlled reaction vessel (see Figs. 3 and 6 for their structures):

20 PIBSA 450 (ex. Italmatch) = 95 g

PIBSA 750 (ex. Italmatch) = 83 g

Pentasize 68 (an alkenyl succinate surfactant, ex. Pentagon Chemicals) = 59 g

PEG 200 (ex. Dow) = 122 g

PEG 600 (ex. BASF) = 66 g

25 Trimellitic anhydride (ex. Connect Chemicals) = 14 g

RO5030 (an alcohol ethoxylate surfactant, ex. Ecogreen Chem) = 19 g

p-Toluene sulphonic acid (a reaction catalyst, ex. Sigma-Aldrich) = 2 g

The reaction mixture was then heated to 190 °C until an acid value of approximately 10.0 was achieved. At this point the reaction mixture was cooled to room temperature to give the final
30 polymeric emulsifier product.

EXAMPLE 3

A polymeric lubricant was prepared as follows. The following reagents were added to a stirred, temperature controlled reaction vessel (see Figs. 3 and 6 for their structures):

PIBSA 450 (ex. Italmatch) = 306 g

PEG 200 (ex. Dow) = 608 g

Citric acid (ex. Sigma-Aldrich) = 56 g

RO5030 (ex. Ecogreen Chem) = 76 g

p-Toluene sulphonic acid (a reaction catalyst. ex. Sigma-Aldrich) = 4 g

- 5 The reaction mixture was then heated to 190 °C until an acid value of approximately 4.0 was achieved. At this point the reaction mixture was cooled to room temperature to give the final polymeric lubricant product.

EXAMPLE 4

- Example formulations. This example illustrates the polymeric emulsifier from
10 Example 2 versus a comparative tradition emulsifier. The following emulsions were prepared:

Part 1: Oil based concentrates:

Emulsifier = 20 g

- 15 Example 2 polymeric emulsifier

TOFA/KOH soap traditional emulsifier

Naphthenic base oil (ex. Afton stock) = 79.8 g

Monoisopropanolamine (ex. Sigma-Aldrich; neutralization amine) = 0.2 g

- 20 Part 2: Milky emulsion formation

Oil based concentrate part 1 = 5 g

Water of differing hardness = 95 g

Demineralized water

200 ppm as calcium carbonate

- 25 500 ppm as calcium carbonate

5,000 ppm as Mg^{2+}

5,000 ppm as Ca^{2+}

- Ten milky emulsions in total were prepared. The emulsions were tested for foaming
30 and hard water stability using the following tests:

1. CNOMO foaming test. The milky emulsion was circulated by a pump at a rate of 4 L per minute. The volume of foam obtained after 30 minutes was determined. The test was stopped if the volume of foam reached the 2000 ml maximum before 30 minutes. 50 ppm as $CaCO_3$ samples was tested.

2. Hard water stability. This test was in two parts:

First, the ability of the part 2 milky emulsion to form when the part 1 oil based concentrate was added to water of varying hardness, on initial mixing (0 h). Possible results were as follows:

- 5 a. Emulsion: an opaque milky emulsion formed.
- b. Insoluble: an emulsion did not form. The part 1 oil based concentrate and water appear to form two separate layers.

Second, the presence of any “cream/oil” or “scum” (i.e., precipitation) formation in the emulsion after 24 hours is noted (24 h).

10 Results were as follows

Table 1

Water type	CNOMO test TOFA/KOH	CNOMO test Example 2 polymeric emulsifier	Hard water stability TOFA/KOH	Hard water stability Example 2 polymeric emulsifier
50 ppm as CaCO ₃	Foam volume = 2000ml after 2 minutes. Test failed.	Foam volume = 1700 ml, after 30 minutes. Test passed.		
Demineralized water			0 h = Emulsion; 24 h = 1.0 ml oily cream	0 h = Emulsion 24 h = 0.5 ml oily cream
200 ppm as CaCO ₃			0 h = Emulsion; 24 h = Emulsion, with 1.0 ml oily cream and LIGHT scum	0 h = Emulsion; 24 h = Emulsion with 0.5 ml oily cream and NO scum
500 ppm as CaCO ₃			0 h = Emulsion, 24 h = Emulsion with 1.0 ml oily cream and MODERATE scum	0 h = Emulsion, 24 h = Emulsion with 0.5 ml oily cream and NO scum
5,000 ppm Ca ²⁺			0 h = Insoluble, 5 ml oily cream; 24 h = Insoluble, 5 ml oily cream	0 h = Emulsion; 24 h = Emulsion with 0 ml oily cream and NO scum
5,000 ppm Mg ²⁺			0 h = Insoluble, 5 ml oily cream	0 h = Emulsion; 24 h =

			24 h = Insoluble, 5 ml oily cream	Emulsion with 0 ml oily cream and NO scum
--	--	--	---	---

EXAMPLE 5

This comparative example illustrates a semi-synthetic metal working fluid containing polymeric lubricant from Example 3 versus a traditional semi-synthetic metal working fluid.

5 A finished semi-synthetic metal working fluid was prepared from a pre-made package “Polartech 8123” (boron containing, naphthenic oil based) as follows:

1. Polartech 8123 50%, demineralized water 50%
2. Polartech 8123 45%, demineralized water 50%, example 2 polymeric lubricant 5%.

10 Polartech 8123 is commercially available. The lubricity of the fluids was determined by their ability to reduce tool wear on a machine tool milling titanium based blocks as follows:

Process: down-milling.

15 Metal: Ti-6Al-4V in the beta annealed condition.

Machine: Mori-Seiki SV500.

Tool: Sandvik Coromant CoroMill Plura 16 mm endmill (WC/Co matrix), reground and uncoated

20 Milling process: Radial entry onto “straight line” shoulder mill cuts; cutting speed = 110 m/min

The time taken, in minutes, for the tool to reach 0.2 mm of wear was taken as a measure of the lubricity of the fluid. The longer the time taken, the more lubricous the fluid. Lubricity results are as follows:

25

Table 2

Metal working fluid	Time taken (minutes) for 0.2 mm of tool wear @ 110 m/min
Polartech 8123 only	61
Example 3, polymeric lubricant 5%	142

The results in Table 2 demonstrate the enhance tool life obtained in the presence of the Example 3 polymeric lubricant.

While several embodiments of the present invention have been described and illustrated herein, those of ordinary skill in the art will readily envision a variety of other means and/or structures for performing the functions and/or obtaining the results and/or one or more of the advantages described herein, and each of such variations and/or modifications is deemed to be within the scope of the present invention. More generally, those skilled in the art will readily appreciate that all parameters, dimensions, materials, and configurations described herein are meant to be exemplary and that the actual parameters, dimensions, materials, and/or configurations will depend upon the specific application or applications for which the teachings of the present invention is/are used. Those skilled in the art will recognize, or be able to ascertain using no more than routine experimentation, many equivalents to the specific embodiments of the invention described herein. It is, therefore, to be understood that the foregoing embodiments are presented by way of example only and that, within the scope of the appended claims and equivalents thereto, the invention may be practiced otherwise than as specifically described and claimed. The present invention is directed to each individual feature, system, article, material, kit, and/or method described herein. In addition, any combination of two or more such features, systems, articles, materials, kits, and/or methods, if such features, systems, articles, materials, kits, and/or methods are not mutually inconsistent, is included within the scope of the present invention.

All definitions, as defined and used herein, should be understood to control over dictionary definitions, definitions in documents incorporated by reference, and/or ordinary meanings of the defined terms.

The indefinite articles “a” and “an,” as used herein in the specification and in the claims, unless clearly indicated to the contrary, should be understood to mean “at least one.”

The phrase “and/or,” as used herein in the specification and in the claims, should be understood to mean “either or both” of the elements so conjoined, i.e., elements that are conjunctively present in some cases and disjunctively present in other cases. Multiple elements listed with “and/or” should be construed in the same fashion, i.e., “one or more” of the elements so conjoined. Other elements may optionally be present other than the elements specifically identified by the “and/or” clause, whether related or unrelated to those elements specifically identified. Thus, as a non-limiting example, a reference to “A and/or B”, when used in conjunction with open-ended language such as “comprising” can refer, in one embodiment, to A only (optionally including elements other than B); in another embodiment,

to B only (optionally including elements other than A); in yet another embodiment, to both A and B (optionally including other elements); etc.

As used herein in the specification and in the claims, “or” should be understood to have the same meaning as “and/or” as defined above. For example, when separating items in a list, “or” or “and/or” shall be interpreted as being inclusive, i.e., the inclusion of at least one, but also including more than one, of a number or list of elements, and, optionally, additional unlisted items. Only terms clearly indicated to the contrary, such as “only one of” or “exactly one of,” or, when used in the claims, “consisting of,” will refer to the inclusion of exactly one element of a number or list of elements. In general, the term “or” as used herein shall only be interpreted as indicating exclusive alternatives (i.e. “one or the other but not both”) when preceded by terms of exclusivity, such as “either,” “one of,” “only one of,” or “exactly one of.” “Consisting essentially of,” when used in the claims, shall have its ordinary meaning as used in the field of patent law.

As used herein in the specification and in the claims, the phrase “at least one,” in reference to a list of one or more elements, should be understood to mean at least one element selected from any one or more of the elements in the list of elements, but not necessarily including at least one of each and every element specifically listed within the list of elements and not excluding any combinations of elements in the list of elements. This definition also allows that elements may optionally be present other than the elements specifically identified within the list of elements to which the phrase “at least one” refers, whether related or unrelated to those elements specifically identified. Thus, as a non-limiting example, “at least one of A and B” (or, equivalently, “at least one of A or B,” or, equivalently “at least one of A and/or B”) can refer, in one embodiment, to at least one, optionally including more than one, A, with no B present (and optionally including elements other than B); in another embodiment, to at least one, optionally including more than one, B, with no A present (and optionally including elements other than A); in yet another embodiment, to at least one, optionally including more than one, A, and at least one, optionally including more than one, B (and optionally including other elements); etc.

When the word “about” is used herein in reference to a number, it should be understood that still another embodiment of the invention includes that number not modified by the presence of the word “about.”

It should also be understood that, unless clearly indicated to the contrary, in any methods claimed herein that include more than one step or act, the order of the steps or acts

of the method is not necessarily limited to the order in which the steps or acts of the method are recited.

- In the claims, as well as in the specification above, all transitional phrases such as “comprising,” “including,” “carrying,” “having,” “containing,” “involving,” “holding,” “composed of,” and the like are to be understood to be open-ended, i.e., to mean including but not limited to. Only the transitional phrases “consisting of” and “consisting essentially of” shall be closed or semi-closed transitional phrases, respectively, as set forth in the United States Patent Office Manual of Patent Examining Procedures, Section 2111.03.
- 5

CLAIMS

What is claimed is:

1. A composition, comprising:
 - 5 a molecular compound comprising at least:
 - (a) a first portion derived from one or more polydentate acids or polydentate acid derivatives that are capable of forming at least three ester groups;
 - (b) a second portion derived from one or more polyalkylene glycols; and
 - (c) a third portion derived from one or more anhydrides or derivatives
 - 10 thereof, wherein the one or more anhydrides or derivatives thereof are other than polydentate acids or polydentate acid derivatives that are capable of forming at least three ester groups; and
 - wherein the first portion is covalently bonded to the second portion, and the second portion is covalently bonded to the third portion.
- 15 2. The composition of claim 1, wherein the first portion is derived from at least one or more of trimellitic acid, trimellitic anhydride, citric acid, and citric anhydride.
3. The composition of any preceding claim, wherein the second portion is derived from
- 20 one or more polyethylene glycols.
4. The composition of any preceding claim, wherein the second portion is derived from at least one difunctional polyalkylene glycol, preferably at least two difunctional polyalkylene glycols.
- 25 5. The composition of any preceding claim, wherein the second portion is derived from at least one monofunctional polyalkylene glycol.
6. The composition of any preceding claim, wherein the molecular compound further
- 30 comprises a portion derived from a non-alkoxylated alcohol, preferably wherein the non-alkoxylated alcohol is monofunctional or polyfunctional.

7. The composition of any preceding claim, wherein the third portion is derived from at least one of succinic anhydride, alkyl succinic anhydride, and alkenyl succinic anhydride.
- 5 8. The composition of any preceding claim, wherein the third portion is derived from at least one PIBSA, preferably at least two PIBSAs, preferably wherein the at least two PIBSA components are of different molecular weight.
9. The composition of any preceding claim, wherein the third portion is derived from at least one alkyl or alkenyl succinic anhydride other than PIBSA.
- 10 10. The composition of any preceding claim, wherein the second portion is derived from at least two difunctional polyalkylene glycol components and at least one monofunctional polyalkylene glycol, and wherein the at least two difunctional polyalkylene glycol derivatives are of different molecular weight or are different polyalkylene glycols.
- 15 11. The composition of any preceding claim, wherein the overall mole ratio of the third portion to the first portion is between 1:1 and 10:1, preferably between 4:1 and 8:1; and/or wherein the overall mole ratio of the second portion to the third portion is between 0.5:1 and 10:1, preferably between 1:1 and 5:1; and/or wherein the overall mole ratio of the second portion to the first portion is between 1:1 and 15:1, preferably between 6:1 and 14:1.
- 20 12. A composition, comprising:
a molecular compound comprising at least:
(a) a first portion derived from a polydentate acid or a polydentate acid derivative, wherein the polydentate acid comprises three or more -COOH moieties;
(b) a second portion derived from polyalkylene glycol; and
(c) a third portion derived from an anhydride or derivative thereof;
wherein the first portion is covalently bonded to the second portion, and the second portion is covalently bonded to the third portion.
- 25

13. The composition of claim 12, wherein at least one first portion is derived from one or more of trimellitic acid, trimellitic anhydride, citric acid, or citric anhydride;
and/or
5 wherein at least one second portion is derived from polyethylene glycol;
and/or
wherein at least one third portion is derived from succinic anhydride, alkyl succinic anhydride, and/or alkenyl succinic anhydride.
- 10 14. The composition of any one of claims 12 or 13, wherein the composition comprises more than one first portion, more than one second portion, and/or more than one third portion.
- 15 15. The composition of any preceding claim, wherein the compound has an M_w of at least 1000 daltons, preferably between 1000 and 100,000 daltons, more preferably between 2000 and 20,000 daltons, even more preferably between 3000 and 5000 daltons, or between 5000 and 15,000 daltons or between 5000 and 50,000 daltons.
- 20 16. The composition of any preceding claim, wherein the composition complies with one or more of the following (i) or (ii):
(i) wherein the compound has an HLB of less than 18, wherein the compound has an HLB of between 2 and 16, or wherein the compound has an HLB of less than 14, preferably wherein the compound has an HLB of less than 12, preferably wherein the HLB is determined by Griffin's method; and/or
25 (ii) wherein the compound has an acid value of between 2 mg KOH/g and 40 mg KOH/g, preferably between 5 mg KOH/g and 20 mg KOH/g, more preferably between 6 mg and 16 mg KOH/g, or wherein the compound has an acid value of between 1 mg KOH/g and 20 mg KOH/g, preferably between 2 mg and 12 mg KOH/g, preferably wherein the acid value is determined via ASTM D974.
- 30 17. The composition of any preceding claim, wherein the composition is a metalworking fluid, optionally further comprising at least water and/or an oil, preferably wherein the metalworking fluid is a semi-synthetic metalworking fluid.

18. A method of producing a composition according to any preceding claim, the method comprising:
- 5 reacting (i) a polydentate acid and/or polydentate acid derivative, (ii) an anhydride and/or an anhydride derivative, and (iii) a polyalkylene glycol and/or an ethoxylated alcohol to produce a product, wherein the polydentate acid and/or polydentate acid derivative is capable of forming at least three ester groups.
19. The method of claim 18, wherein the method comprises:
- 10 reacting the anhydride and/or an anhydride derivative, and the polyalkylene glycol and/or the ethoxylated alcohol to produce an intermediate; and
- reacting the intermediate with the polydentate acid and/or the polydentate acid derivative to produce the product,
- wherein the polydentate acid and/or polydentate acid derivative is selected from the group consisting of trimellitic acid, trimellitic anhydride and citric acid, and
- 15 wherein the anhydride is derived from succinic anhydride, alkenyl succinic anhydride, and/or alkyl succinic anhydride.
20. The method of claim 18 or 19, wherein the polydentate acid and/or the polydentate acid derivative and the polyalkylene glycol and/or the ethoxylated alcohol react via an esterification reaction.
- 20
21. The method of any one of claims 18-20, comprising heating the reaction mixture to at least 160 °C, preferably to at least 180 °C, and/or to no more than 230 °C.
22. The method of any one of claims 18-21, wherein the composition complies with one or more of the following (i) – (ii):
- 25 (i) comprising reacting until the product has an acid value of at least 4 mg KOH/g, preferably until the product has an acid value of at least 12 mg KOH/g; and/or
- 30 (ii) wherein the reacting occurs under vacuum or under nitrogen.
23. A composition, comprising:
- a compound formed by a method comprising covalently bonding a polydentate acid and/or polydentate acid derivative, a polyalkylene glycol and/or an ethoxylated

alcohol, and an anhydride and/or an anhydride derivative to form the compound, preferably via an esterification reaction, optionally wherein the method is the method according to any one of claims 18-22.

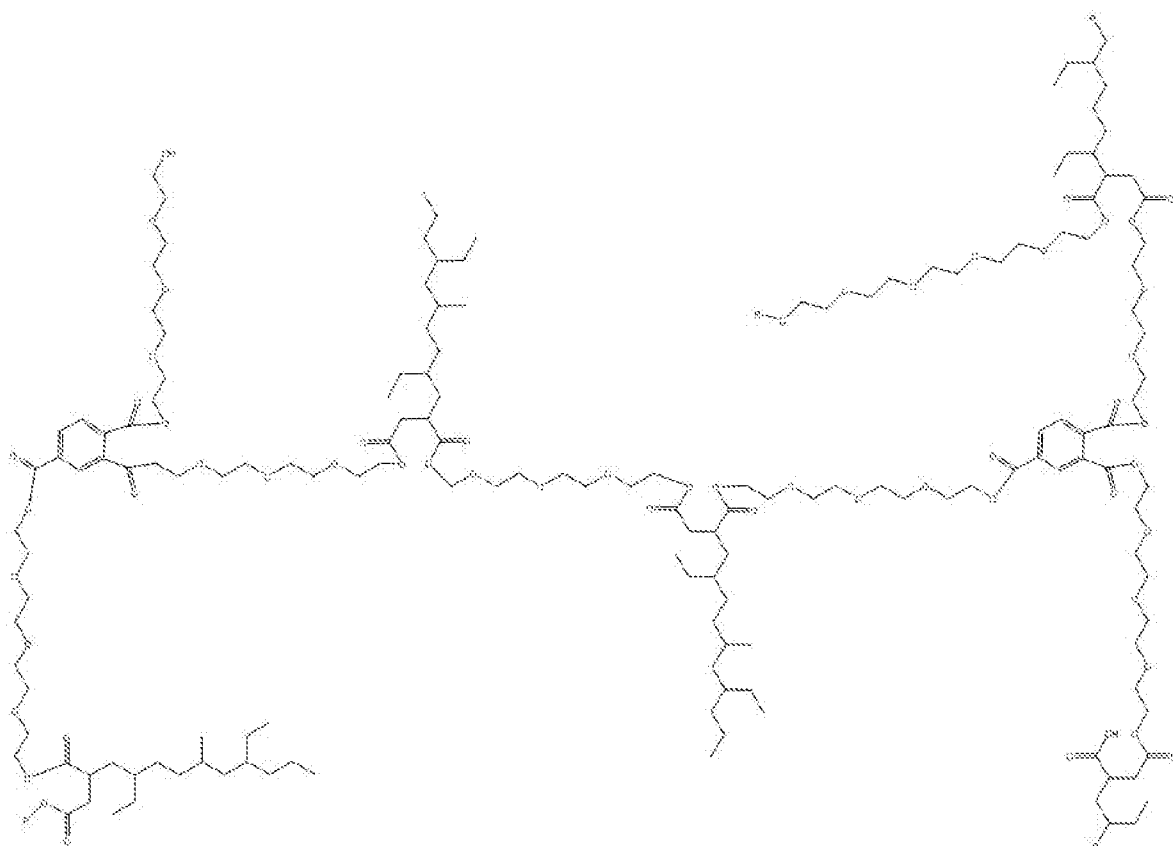


FIG. 1

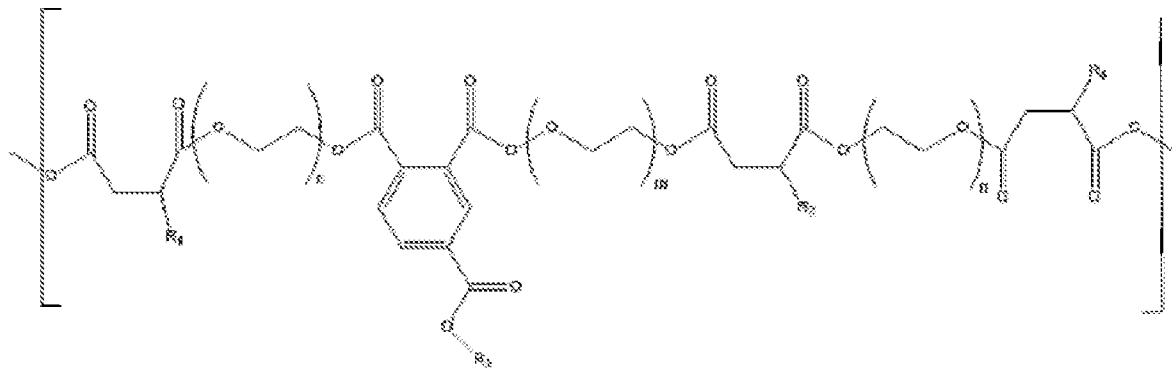


FIG. 2

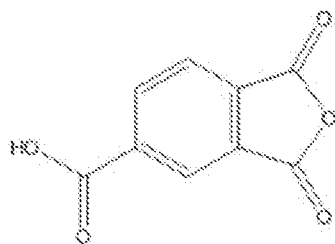


FIG. 3

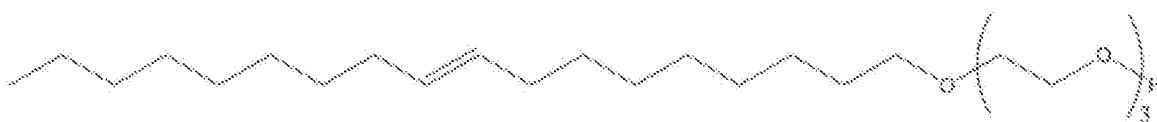


FIG. 4A

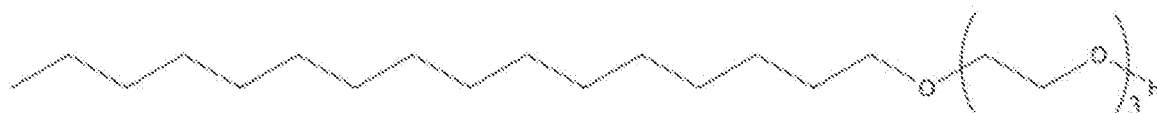


FIG. 4B

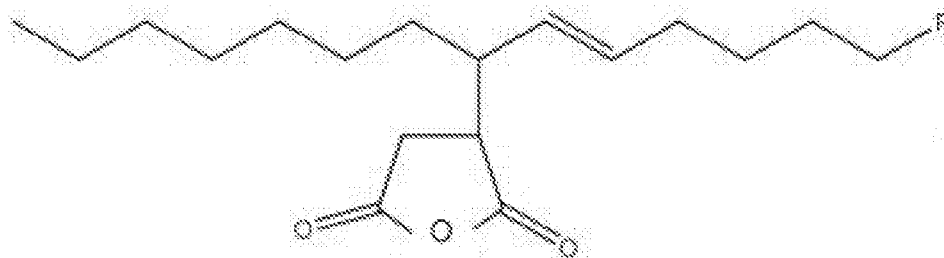


FIG. 5

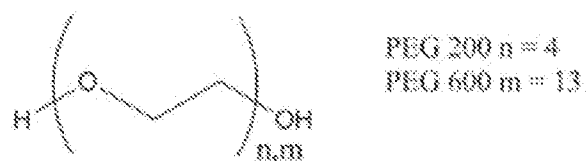


FIG. 6A

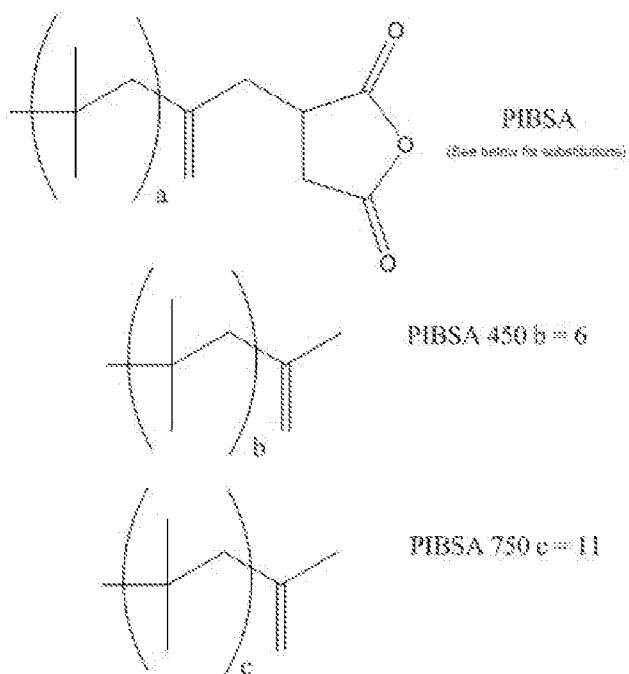


FIG. 6B

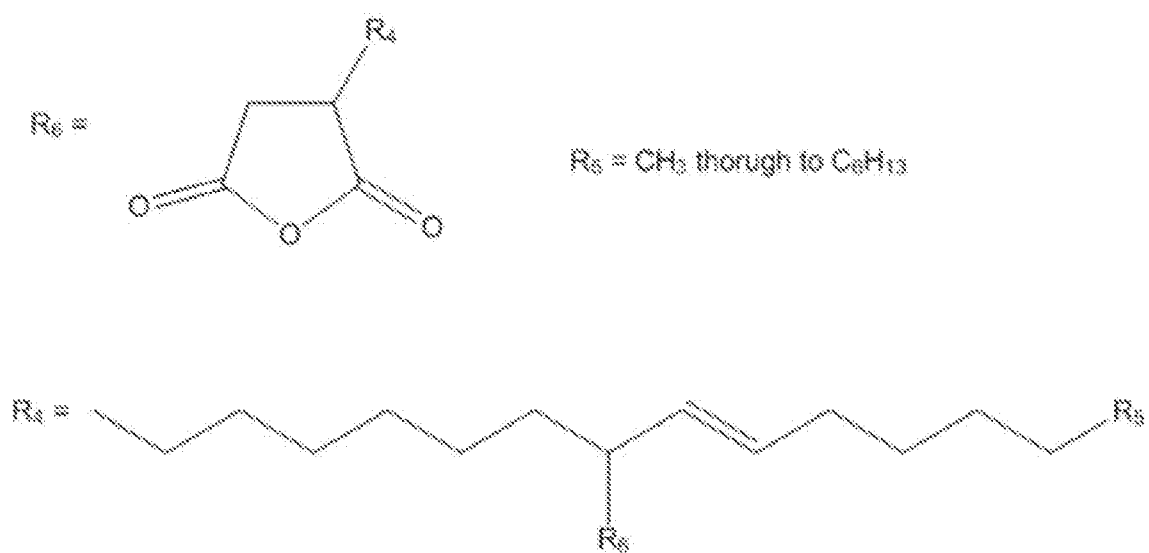


FIG. 6C

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US16/69107

A. CLASSIFICATION OF SUBJECT MATTER

IPC - C07C 69/40, 69/704, 59/265, 55/10; C08F 2/22; C08K 5/10; C10M 145/06, 145/16 (2017.01)
 CPC - C07C 69/40, 69/704, 59/265, 55/10; C08F 2/22; C08K 5/10; C10M 145/06, 145/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

See Search History document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

See Search History document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2008/0242790 A1 (LEYRER, RJ et al.) 02 October 2008; paragraphs [0013], [0072], [0180], [0182], [0184], [0214]	1-2, 3/1-2, 12-13, 14/12-13
Y	US 2004/0159823 A1 (MANOS, PD) 19 August 2004; paragraphs [0020], [0053]-[0054], [0073]-[0074]; claim 63	1-2, 3/1-2, 12-13, 14/12-13
Y	US 2013/0281634 A1 (HARRIS, JM et al.) 24 October 2013; paragraphs [0003], [0076]-[0077]	1-2, 3/1-2, 12-13, 14/12-13
A	US 2007/0072778 A1 (KALHAN, S et al.) 29 March 2007; entire document	1-2, 3/1-2, 12-13, 14/12-13

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

10 February 2017 (10.02.2017)

Date of mailing of the international search report

08 MAR 2017

Name and mailing address of the ISA/

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
 P.O. Box 1450, Alexandria, Virginia 22313-1450
 Facsimile No. 571-273-8300

Authorized officer

Shane Thomas

PCT Helpdesk: 571-272-4300
 PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US16/69107

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 4-11, 15-23
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.