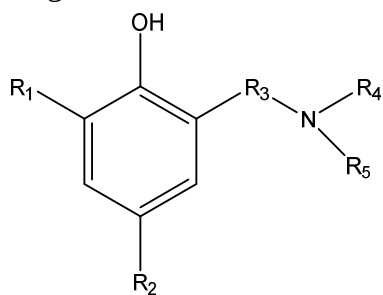


## SUMMARY

**[0004]** In one example or approach, a fuel additive or fuel additive package for a spark-ignition engine is described herein to provide improved engine performance and includes a Mannich detergent including the reaction product of a hydrocarbyl-substituted phenol or cresol, one or more aldehydes, and one or more amines; a succinimide detergent prepared by reacting a hydrocarbyl-substituted succinic acylating agent with an amine, polyamine, or alkyl amine having one or more primary, secondary, or tertiary amino groups; and wherein a weight ratio of the Mannich detergent to the succinimide detergent is from about 15:1 to about 30:1. As discussed more herein, such weight ratios provide a synergistic effect with improved engine and/or injector performance in both port fuel injection (PFI) engines as well as gasoline direct injection (GDI) engines.

**[0004a]** In one aspect, the present disclosure refers to a fuel additive for a spark-ignition engine comprising: a Mannich detergent including the reaction product of a hydrocarbyl-substituted phenol or cresol, one or more aldehydes, and one or more amines; a succinimide detergent prepared by reacting a hydrocarbyl-substituted succinic acylating agent with an amine, polyamine, or alkyl amine having one or more primary, secondary, or tertiary amino groups; and wherein a weight ratio of the Mannich detergent to the succinimide detergent is from about 15:1 to about 30:1.

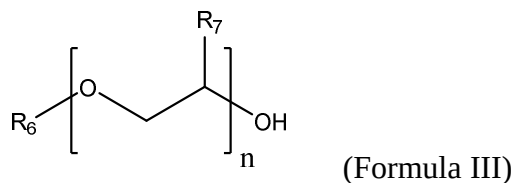
**[0005]** In other examples or approaches, the fuel additive of the previous paragraphs may include one or more optional features or examples in any combination. The optional features or examples may include one or more of the following: wherein the weight ratio of the Mannich detergent to the succinimide detergent is from about 20:1 to about 30:1; and/or wherein the Mannich detergent has the structure of Formula I:



(Formula I)

wherein R<sub>1</sub> of Formula I is hydrogen or a C1 to C4 alkyl group, R<sub>2</sub> of Formula I is a hydrocarbyl group having a molecular weight of about 500 to about 3000, R<sub>3</sub> of Formula I is a C1 to C4 alkylene or alkenyl group (preferably a C1 group), and R<sub>4</sub> and R<sub>5</sub> of Formula I are, independently, hydrogen, a linear or branched C1 to C12 alkyl group, or a mono or di(C1 to C4)alkyl amino C1-C12 alkyl group; and/or wherein R<sub>2</sub> of Formula I is polyisobutenyl having a number average molecular weight of about 500 to about 1500; and/or wherein the succinimide detergent is a hydrocarbyl substituted mono-succinimide detergent, a hydrocarbyl substituted bis-succinimide detergent, or a combination thereof; and/or wherein the hydrocarbyl-substituted succinic acylating agent is a hydrocarbyl-substituted succinic anhydride, wherein the

hydrocarbyl group has a molecular weight of about 450 to about 3000, and wherein a molar ratio of the hydrocarbyl-substituted succinic anhydride to the amine, polyamine, or alkyl amine is from about 0.5:1 to about 2:1; and/or wherein the hydrocarbyl-substituted succinic anhydride is polyisobutylene substituted succinic anhydride, and wherein the polyisobutylene has a number average molecular weight of about 500 to about 1200 as measured by GPC using polystyrene as reference; and/or wherein the amine, polyamine, or alkyl amine is tetraethylene pentamine (TEPA), triethylene tetraamine (TETA), or a polyamine or alkyl amine having the formula  $H_2N-((CHR_{20}-(CH_2)_q-NH)_r-H$ , wherein  $R_{20}$  thereof is hydrogen or an alkyl group having from 1 to 4 carbon atoms, q is an integer of from 1 to 4 and r is an integer of from 1 to 6, and mixtures thereof; and/or wherein the amine, polyamine, or alkyl amine is tetraethylene pentamine (TEPA); and/or further comprising an alkoxyated alcohol, and wherein a weight ratio of the alkoxyated alcohol to the Mannich detergent is about 1.0 or less (preferably 0.8 or less, 0.6 or less, or 0.5 or less); and/or wherein the alkoxyated alcohol is a polyether prepared by reacting an alkyl alcohol or an alkylphenol with an alkylene oxide selected from ethylene oxide, propylene oxide, butylene oxide, copolymers thereof, or combinations thereof; and/or wherein the alkoxyated alcohol is a polyether having the structure of Formula III:



wherein  $R_6$  of Formula III is an aryl group or a linear, branched, or cyclic aliphatic group having 5 to 50 carbons,  $R_7$  of Formula III is a C1 to C4 alkyl group, and n is an integer from 5 to 100; and/or wherein the fuel additive includes about 20 to about 60 weight percent of the Mannich detergent, about 0.5 to about 10 weight percent of the succinimide detergent, and about 5 to about 30 weight percent of an alkoxyated alcohol.

**[0006]** In another approach or example, a gasoline fuel composition providing improved engine and/or injector performance in both port fuel injection (PFI) engines as well as gasoline direct injection (GDI) engines is described herein. The gasoline fuel composition includes about 15 to about 300 ppmw of a Mannich detergent including the reaction product of a hydrocarbyl-substituted phenol or cresol, one or more aldehydes, and one or more amines; about 0.5 to about 20 ppmw of a succinimide detergent prepared by reacting a hydrocarbyl-substituted succinic acylating agent with an amine, polyamine, or alkyl amine having one or more primary,

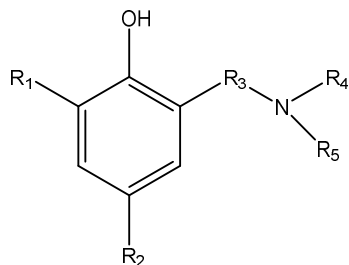
secondary, or tertiary amino groups; wherein a weight ratio of the Mannich detergent to the succinimide detergent is from about 15:1 to about 30:1; and about 5 to about 150 ppmw of an alkoxyated alcohol. In further examples, the gasoline fuel composition may also include any of the optional features or examples as described above with respect to the fuel additive.

**[0006a]** In one aspect, the present disclosure refers to a gasoline fuel composition comprising about 15 to about 300 ppmw of a Mannich detergent including the reaction product of a hydrocarbyl-substituted phenol or cresol, one or more aldehydes, and one or more amines; about 0.5 to about 20 ppmw of a succinimide detergent prepared by reacting a hydrocarbyl-substituted succinic acylating agent with an amine, polyamine, or alkyl amine having one or more primary, secondary, or tertiary amino groups; wherein a weight ratio of the Mannich detergent to the succinimide detergent is about from 15:1 to about 30:1; and about 5 to about 150 ppmw of an alkoxyated alcohol.

**[0007]** In yet other approaches or examples, a method of reducing deposits in a gasoline engine is described herein. The method includes operating a gasoline engine on a fuel composition containing a major amount of a gasoline fuel and a minor amount of a fuel additive by injecting the gasoline fuel through one or more injectors; wherein the fuel additive includes (i) a Mannich detergent including the reaction product of a hydrocarbyl-substituted phenol or cresol, one or more aldehydes, and one or more amines; (ii) a succinimide detergent prepared by reacting a hydrocarbyl-substituted succinic acylating agent with an amine, polyamine, or alkyl amine having one or more primary, secondary, or tertiary amino groups; and (iii) wherein the fuel additive has a weight ratio of the Mannich detergent to the succinimide detergent of about 15:1 to about 30:1; and wherein the fuel additive reduces deposits in the gasoline engine.

**[0007a]** In one aspect, the present disclosure refers to a method of reducing deposits in a gasoline engine, the method comprising: operating a gasoline engine on a fuel composition containing a major amount of a gasoline fuel and a minor amount of a fuel additive by injecting the gasoline fuel through one or more injectors; wherein the fuel additive includes (i) a Mannich detergent including the reaction product of a hydrocarbyl-substituted phenol or cresol, one or more aldehydes, and one or more amines; (ii) a succinimide detergent prepared by reacting a hydrocarbyl-substituted succinic acylating agent with an amine, polyamine, or alkyl amine having one or more primary, secondary, or tertiary amino groups; and (iii) wherein the fuel additive has a weight ratio of the Mannich detergent to the succinimide detergent of from about 15:1 to about 30:1; and wherein the fuel additive reduces deposits in the gasoline engine.

**[0008]** In other examples or approaches, the method described in the previous paragraphs may be include one or more optional features, method steps, or examples in any combination. The optional features, steps, or examples may include one or more of the following: wherein the fuel additive reduces deposits in a port fuel injection (PFI) engine, a gasoline direct injection (GDI) engine, or both; and/or wherein the reduced deposits are reduced injector deposits measured by one of injector pulse width, injection duration, injector flow, or combinations thereof; and/or wherein the fuel additive reduces deposits when sprayed from an injector configured to spray droplets of about 10 to about 30 microns, about 120 to about 200 microns, or both; and/or wherein the weight ratio of the Mannich detergent to the succinimide detergent is from about 20:1 to about 30:1; and/or wherein the Mannich detergent has the structure of Formula I:



(Formula I)

detergent, about 0.5 to about 10 weight percent of the succinimide detergent, and about 5 to about 30 weight percent of the alkoxyated alcohol.

**[0009]** In yet other approaches or examples, the use of a fuel additive package as described by any example herein or the use of a gasoline fuel as described by any example of the fuel composition herein for improving the injector performance of a port fuel injection (PFI) engine, a gasoline direct injection (GDI) engine, or both the PFI and GDI engine.

**[00010]** In any example of the fuel additive package, the fuel, the method, or the use herein, the fuel additive package of this disclosure may be free of quaternary ammonium salt detergents, and preferably, free of quaternary ammonium internal salt detergents that are obtained from amines or polyamines and substantially devoid of any free anion species. In this context, free of means less than 0.5 ppmw, less than 0.1 ppmw, less than 0.05 ppmw or, preferably, none.

#### BRIEF DESCRIPTION OF DRAWING FIGURES

**[00011]** FIG. 1 is a graph showing GDI dirty-up (DU) and clean-up (CU) of Comparative and Inventive fuel additives; and

**[00012]** FIG. 2 is a graph showing GDI dirty-up (DU) and clean-up (CU) of Comparative and Inventive fuel additives.

#### DETAILED DESCRIPTION

**[00013]** The present disclosure provides fuel additives including combinations of Mannich detergent(s) and succinimide detergent(s) discovered effective in certain weight ratios to provide improved engine and/or injector performance in both port fuel injection (PFI) engines as well as gasoline direct injection (GDI) engines. The fuel additives, in some approaches, may also include alkoxyated alcohols and, when included, certain ratios of the alkoxyated alcohol to the Mannich detergent. Also provided herein are fuel compositions including the novel fuel additive combinations and methods of using or combusting a fuel including the fuel additive combinations herein to achieve improved engine, intake valve, and/or injector performance. As noted more below, the fuel additives herein include a synergistic combination of Mannich detergent(s) and succinimide detergent(s) when used in a weight ratio of the Mannich detergent to the succinimide detergent of about 15:1 to about 30:1. Mannich detergents alone do not