Adjuvants, in the form of solids or liquids, can be added directly to a formulated agricultural product, such as a granule, to provide improved performance of the product upon application. Commonly used adjuvants may include, for example, surfactants, spreaders, petroleum and plant derived oils and solvents and wetting agents. Examples of commonly used adjuvants include, but are not limited to, paraffin oil, horticultural spray oils (*e.g.*, summer oil), methylated rape seed oil, methylated soybean oil, highly refined vegetable oil and the like, polyol fatty acid esters, polyethoxylated esters, ethoxylated alcohols, alkyl polysaccharides and blends, amine ethoxylates, sorbitan fatty acid ester ethoxylates, polyethylene glycol esters, organosilicone based surfactants, ethylene vinyl acetate terpolymers, ethoxylated alkyl aryl phosphate esters and the like. These and other adjuvants are described in the "*Compendium of Herbicide Adjuvants, 9th Edition,*" edited by Bryan Young, Dept. of Plant, Soil and Agricultural Systems, Southern Illinois University MC-4415, 1205 Lincoln Drive, Carbondale, IL 62901, which is available for viewing on the internet at http://www.herbicide-adjuvants.com/.

The term "built-in adjuvant" refers to one or more adjuvants that have been added to a particular formulation, such as a granule or liquid formulation, at the manufacturing stage of the product, rather than at the point of use of the product such as, for example, to a spray solution. The use of built-in adjuvants simplifies the use of agrochemical products for the end-user by reducing the number of ingredients that must be individually measured and applied.

The built-in adjuvants of the described improved solid herbicidal compositions can be in the form of a liquid or a solid, and may include one or more of a non-ionic surfactant or a water immiscible liquid. In one embodiment, the built-in adjuvant of the described improved solid herbicidal compositions is one or more of water-immiscible liquid. In one embodiment, the built-in adjuvant of the described improved solid herbicidal compositions is one or more of non-ionic surfactant.

Non-ionic surfactants that may be used as built-in adjuvants include, but are not limited to, polyol fatty acid esters, polyethoxylated esters, polyethoxylated alcohols, alkyl polysaccharides such as alkyl polyglycosides and blends thereof, amine ethoxylates, sorbitan fatty acid ester ethoxylates, organosilicone based surfactants, ethylene vinyl acetate terpolymers, ethoxylated alkyl aryl phosphate esters and sucrose esters of fatty acids.

Water immiscible liquids that may be used as built-in adjuvants generally have less than about 1 volume per cent solubility in water and may include, but are not limited to, petroleum fractions or hydrocarbons such as mineral oil, kerosene, paraffinic oils, mixed naphthalene and alkyl naphthalene fractions, aromatic solvents, particularly alkyl substituted benzenes such as xylene or propylbenzene fractions, and the like; plant derived oils such as soybean oil, rape seed oil, olive oil, castor oil, sunflower seed oil, coconut oil, corn oil, cotton seed oil, linseed oil, palm oil, peanut oil, safflower oil, sesame oil, tung oil and the like; esters of the above plant derived oils such as 2-ethyl hexyl stearate, *n*-butyl oleate, isopropyl myristate, propylene glycol dioleate and the like; and esters of diacids such as di-octyl succinate, di-butyl adipate, di-octyl phthalate, ditridecyl phthalate and the like.

In certain embodiments, built-in adjuvants include one or more of petroleum fractions or hydrocarbons such as mineral oil, paraffinic oils and aromatic solvents like xylene, propylbenzene fractions, alkyl naphthalene fractions, and the like; plant derived oils such as soybean oil, rape seed oil, olive oil, castor oil, sunflower seed oil, coconut oil, corn oil, cotton seed oil, linseed oil, palm oil, peanut oil, safflower oil, sesame oil, tung oil and the like; C_1-C_6 esters of plant derived oils such as methylated seed oils; esters of diacids such as di-octyl succinate, di-butyl adipate, di-octyl phthalate, ditridecyl phthalate and the like; polyol fatty acid esters, polyethoxylated esters, polyethoxylated alcohols, alkyl polysaccharides such as alkyl polyglycosides and blends thereof, amine ethoxylates, sorbitan fatty acid ester ethoxylates, organosilicone based surfactants, ethylene vinyl acetate terpolymers, ethoxylated alkyl aryl phosphate esters and sucrose esters of fatty acids.

In some embodiments, the built-in adjuvant of the described improved solid herbicidal compositions is one or more of a petroleum derived paraffinic hydrocarbon, a petroleum derived aromatic hydrocarbon, a plant derived oil, or a C_1-C_6 ester of a plant derived oil. In some embodiments, the built-in adjuvant of the described improved solid herbicidal compositions is one or more of a seed oil, or a C_1-C_6 esters of plant derived oil. In some embodiments, the built-in adjuvant of the described improved solid herbicidal compositions is methyl soyate.

In some embodiments, the built-in adjuvants of the described improved solid herbicidal compositions are present in the composition in an amount of from about 50 g/kg to about 750 g/kg, from about 200 g/kg to about 600 g/kg, or from about 300 g/kg to about 600 g/kg relative to the total weight of the composition.

transformations occur are indicative of the relative stability of such compositions. Compositions that have thermal events occurring at lower temperatures are generally less stable than those with thermal events occurring at high temperatures.

E. Methods of preparation

A further aspect of the compositions and methods described herein concerns methods of preparing the improved solid herbicidal compositions. In one embodiment, granule formulations may be produced using one or more of the following processing methods: (1) pan granulation, (2) mixing agglomeration, (3) extrusion granulation, (4) fluid bed granulation, (5) spray granulation or agglomeration, and (6) drum granulation. In some embodiments, granules may be prepared by using a pellet press. The physico-chemical properties of the active ingredient and additives are important to consider when choosing a process to use. G. A. Bell and D. A. Knowles in, "Chemistry and Technology of Agrochemical Formulations," D. A. Knowles, editor, (Kluwer Academic Publishers, 1998), pages 41-114, incorporated herein by reference, describe the types of granules used in agricultural chemical formulations and provide references to the production of these solid formulations. In one embodiment, powder formulations can be produced by vacuum drying, rotary evaporator drying, spray drying, drum drying, or other processing methods that are well known to those of skill in the art.

In any of the processing methods described herein, optional inert ingredients may be added to a composition before, during or after processing to improve the processing or to improve the final quality, stability or dispersion properties in water of the powder or granule. These optional inert ingredients may include, but are not limited to, flowability additives, stability additives such as, for example, antioxidants to stabilize the built-in adjuvant, and anti-caking agents such as, for example, hydrophilic precipitated silicas, hydrophilic fumed silicas and clays, anti-foaming agents, wetting agents, binders, dispersing agents, solid diluents and carriers.

Also provided herein are examples where solid additives are used to stabilize water insoluble liquids during processing to make stable powders. Examples of such additives are gelatin, glycine, casein, water-soluble polymers such as polyvinyl alcohol and polyvinyl pyrrolidone, and polysaccharides. Some of these applications are described, for example, in US 4,244,836 and WO 2006/076943, incorporated herein by reference. There have been,

Adjuvants, in the form of solids or liquids, can be added directly to a formulated agricultural product, such as a granule, to provide improved performance of the product upon application. Commonly used adjuvants may include, for example, surfactants, spreaders, petroleum and plant derived oils and solvents and wetting agents. Examples of commonly used adjuvants include, but are not limited to, paraffin oil, horticultural spray oils (*e.g.*, summer oil), methylated rape seed oil, methylated soybean oil, highly refined vegetable oil and the like, polyol fatty acid esters, polyethoxylated esters, ethoxylated alcohols, alkyl polysaccharides and blends, amine ethoxylates, sorbitan fatty acid ester ethoxylates, polyethylene glycol esters, organosilicone based surfactants, ethylene vinyl acetate terpolymers, ethoxylated alkyl aryl phosphate esters and the like. These and other adjuvants are described in the "*Compendium of Herbicide Adjuvants, 9th Edition,*" edited by Bryan Young, Dept. of Plant, Soil and Agricultural Systems, Southern Illinois University MC-4415, 1205 Lincoln Drive, Carbondale, IL 62901, which is available for viewing on the internet at http://www.herbicide-adjuvants.com/.

The term "built-in adjuvant" refers to one or more adjuvants that have been added to a particular formulation, such as a granule or liquid formulation, at the manufacturing stage of the product, rather than at the point of use of the product such as, for example, to a spray solution. The use of built-in adjuvants simplifies the use of agrochemical products for the end-user by reducing the number of ingredients that must be individually measured and applied.

The built-in adjuvants of the described improved solid herbicidal compositions can be in the form of a liquid or a solid, and may include one or more of a non-ionic surfactant or a water immiscible liquid. In one embodiment, the built-in adjuvant of the described improved solid herbicidal compositions is one or more of water-immiscible liquid. In one embodiment, the built-in adjuvant of the described improved solid herbicidal compositions is one or more of non-ionic surfactant.

Non-ionic surfactants that may be used as built-in adjuvants include, but are not limited to, polyol fatty acid esters, polyethoxylated esters, polyethoxylated alcohols, amine ethoxylates, sorbitan fatty acid ester ethoxylates, organosilicone based surfactants, ethylene vinyl acetate terpolymers, ethoxylated alkyl aryl phosphate esters and sucrose esters of fatty acids.

Water immiscible liquids that may be used as built-in adjuvants generally have less than about 1 volume per cent solubility in water and may include, but are not limited to, petroleum fractions or hydrocarbons such as mineral oil, kerosene, paraffinic oils, mixed naphthalene and alkyl naphthalene fractions, aromatic solvents, particularly alkyl substituted benzenes such as xylene or propylbenzene fractions, and the like; plant derived oils such as soybean oil, rape seed oil, olive oil, castor oil, sunflower seed oil, coconut oil, corn oil, cotton seed oil, linseed oil, palm oil, peanut oil, safflower oil, sesame oil, tung oil and the like; esters of the above plant derived oils such as 2-ethyl hexyl stearate, *n*-butyl oleate, isopropyl myristate, propylene glycol dioleate and the like; and esters of diacids such as di-octyl succinate, di-butyl adipate, di-octyl phthalate, ditridecyl phthalate and the like.

In certain embodiments, built-in adjuvants include one or more of petroleum fractions or hydrocarbons such as mineral oil, paraffinic oils and aromatic solvents like xylene, propylbenzene fractions, alkyl naphthalene fractions, and the like; plant derived oils such as soybean oil, rape seed oil, olive oil, castor oil, sunflower seed oil, coconut oil, corn oil, cotton seed oil, linseed oil, palm oil, peanut oil, safflower oil, sesame oil, tung oil and the like; C_1-C_6 esters of plant derived oils such as methylated seed oils; esters of diacids such as di-octyl succinate, di-butyl adipate, di-octyl phthalate, ditridecyl phthalate and the like; polyol fatty acid esters, polyethoxylated esters, polyethoxylated alcohols, amine ethoxylates, sorbitan fatty acid ester ethoxylates, organosilicone based surfactants, ethylene vinyl acetate terpolymers, ethoxylated alkyl aryl phosphate esters and sucrose esters of fatty acids.

In some embodiments, the built-in adjuvant of the described improved solid herbicidal compositions is one or more of a petroleum derived paraffinic hydrocarbon, a petroleum derived aromatic hydrocarbon, a plant derived oil, or a C_1-C_6 ester of a plant derived oil. In some embodiments, the built-in adjuvant of the described improved solid herbicidal compositions is one or more of a seed oil, or a C_1-C_6 esters of plant derived oil. In some embodiments, the built-in adjuvant of the described improved solid herbicidal compositions is methyl soyate.

In some embodiments, the built-in adjuvants of the described improved solid herbicidal compositions are present in the composition in an amount of from about 50 g/kg to about 750 g/kg, from about 200 g/kg to about 600 g/kg, or from about 300 g/kg to about 600 g/kg relative to the total weight of the composition.

transformations occur are indicative of the relative stability of such compositions. Compositions that have thermal events occurring at lower temperatures are generally less stable than those with thermal events occurring at high temperatures.

E. Methods of preparation

A further aspect of the compositions and methods described herein concerns methods of preparing the improved solid herbicidal compositions. In one embodiment, granule formulations may be produced using one or more of the following processing methods: (1) pan granulation, (2) mixing agglomeration, (3) extrusion granulation, (4) fluid bed granulation, (5) spray granulation or agglomeration, and (6) drum granulation. In some embodiments, granules may be prepared by using a pellet press. The physico-chemical properties of the active ingredient and additives are important to consider when choosing a process to use. G. A. Bell and D. A. Knowles in, "Chemistry and Technology of Agrochemical Formulations," D. A. Knowles, editor, (Kluwer Academic Publishers, 1998), pages 41-114, incorporated herein by reference, describe the types of granules used in agricultural chemical formulations and provide references to the production of these solid formulations. In one embodiment, powder formulations can be produced by vacuum drying, rotary evaporator drying, spray drying, drum drying, or other processing methods that are well known to those of skill in the art.

In any of the processing methods described herein, optional inert ingredients may be added to a composition before, during or after processing to improve the processing or to improve the final quality, stability or dispersion properties in water of the powder or granule. These optional inert ingredients may include, but are not limited to, flowability additives, stability additives such as, for example, antioxidants to stabilize the built-in adjuvant, and anti-caking agents such as, for example, hydrophilic precipitated silicas, hydrophilic fumed silicas and clays, anti-foaming agents, wetting agents, binders, dispersing agents, solid diluents and carriers.

Also provided herein are examples where solid additives are used to stabilize water insoluble liquids during processing to make stable powders. Examples of such additives are gelatin, glycine, casein and water-soluble polymers such as polyvinyl alcohol and polyvinyl pyrrolidone. Some of these applications are described, for example, in US 4,244,836 and WO 2006/076943, incorporated herein by reference. There have been, however, very limited