Spray droplet modifier composition

Field of the invention

The invention relates generally to oil-based liquid concentrates for use in agricultural applications. The invention relates more particularly to formulations that comprise an agent that modifies the viscosity of a sprayable liquid containing the formulation, oil and a dispersing agent.

Background of the invention

In the agrochemical industry, agriculturally-active compounds are often sprayed, normally after dilution in an aqueous spray liquid, onto plants and/or their habitat. When the agricultural sprays are to be directed onto a specific target, the aerial spray or discharge delivery systems are typically mounted on airplanes, tractors, or ground rigs. When applying such formulations, a more or less pronounced drifting of the spray solution containing the active substance(s) may be observed, depending on the wind conditions, nozzle type, and other application parameters such as nozzle pressure, spray boom height and length, and vehicle speed.

The drift of a spray is determined to a great extent by the droplet size distribution of the spray. Mist, or the fine particles-end of the droplet-size spectrum in agricultural sprays (i.e. those less than about 150 μm in diameter), contributes most to drift. While small droplets provide better coverage of a target, much of the active chemical ingredients in a spray can be rendered ineffective or lost due to spray drift because of the inability of the small diameter spray or mist particles to reach and impact upon the intended target (i.e. the crop or field locus). Generally, the smaller the droplets, the longer the residence time in the air and the higher the tendency to evaporate and/or to drift rather than deposit within the field borders.

In addition, the drift of certain agriculturally-active agents, such as pesticides, is a major source of concern in relation to the environmental impact of agriculture on natural ecosystems and urban areas. This drifting material might cause damage to neighbouring crops, and have effects on the local environment (e.g. surface water, non-target flora and fauna) as well as bystanders and occupants in residential areas. Accordingly, there is a need to reduce these drift-induced problems associated with agrochemical application.

Various methods are used to prevent the drifting of the spray outside the field borders. The use of natural or artificial windbreaks is well known. However, it has been described that even when such screens are used, drift can cause deposition of the active substances behind such borders (e.g. Schampheleire, M. *et al*. "Deposition of spray drift behind border structures", *Crop Protection* (2009) 28 1061-1075). Another frequently-used drift mitigation measure is buffer zones, either off-crop or in-crop. A disadvantage of off-crop buffer zones is that part of the field cannot be sown with a crop, an economic cost to the farmer. A disadvantage of in-crop buffer zones is that part of the crop is not protected adequately, resulting in a lower yield and perhaps resistance development. Clearly, this is something farmers want to prevent.

Next to physically limiting spray drift (e.g. using spray shields), it is also possible to alter the structure of the spray cloud so that less drops are prone to drift (i.e. typically those drops under 150 μm). This can be done by choosing different types of nozzles, changing the pressure at which the spray cloud is produced, or by changing the properties of the spray liquid itself. Changing nozzles and/or nozzle pressure is something farmers do not prefer to do because it is time consuming and is an added cost to crop production. Also, the equipment needed on a sprayer to deal with variable application rates is not common. For these reasons, a more acceptable way to optimise a spray cloud so that it generates less drift is by adjusting the properties of the spray liquid.

One solution proposed in the art to reduce mist and chemical drift in aqueous agricultural sprays is to incorporate into the aqueous medium a viscosity modifier. The viscosity modifier increases the average droplet size of the spray cloud by increasing the viscosity of the spray solution. Examples of some commercially-available products that contain viscosity modifiers (which can be added as tank mix adjuvants with pesticide formulations) include Drop Zone™ DC, Pointblank®, Nalco-trol® and Sta-Put® from Helena, and AntiDrift from AmegA Science Inc. In addition, several patents have been published that discuss the use of viscosity modifiers to reduce drift (e.g. US 7341981 and US 6358296).

However, there is a tendency for viscosity modifiers to create extremely large droplets, as well as reducing the fraction below 150 μm when atomising liquids through conventional agricultural hydraulic nozzles. Retention of larger droplets on leaf surfaces may be reduced as the larger droplets are more likely than smaller droplets to run-off, bounce, or shatter and

redistribute to soil. Fewer larger droplets adhering to the leaf surface will reduce overall biological efficacy.

One of the most commonly used viscosity modifiers is guar gum, or its derivatives. Guar gum is traditionally used as a solid additive to an aqueous agricultural spray medium. Although guar gum is often referred to as a cold water swelling polymer, it hydrates in either cold or hot water to give high viscosity solutions. The viscosity development depends, to a certain extent, on particle size, pH, and temperature. Guar gum solutions are stable over the pH range of 4.0 to 10.5.

However, the aqueous hydration of dry, water-soluble polymers such as guar gum and/or its derivatives in an aqueous agricultural spray medium in order to realize drift reduction properties can often be an arduous and frustrating task for the end-user. Insufficient dispersion of powdered guar gum, caused most often by the too rapid addition of the powder to the aqueous medium, or insufficient agitation of the medium during the guar gum addition process, often results in agglomeration or lumps of guar gel. The lumps of guar gel or other inhomogeneity of the mixture can result in difficulty in spraying and loss of drift control. These gel lumps not only cause a lowering of the overall concentrations of dissolved guar gum in the spray medium, and therefore a reduced drift control of the medium, but also result in a medium that will not flow or be readily pumpable and result in plugging of the spray nozzle holes.

The agglomeration can be reduced in many cases by adding the guar gum to the aqueous system very slowly with vigorous agitation. Slow addition, however, substantially reduces the efficiency and speed of the end-user’s processes.

For the above reasons, agricultural end-users, such as farmers, continue to desire a fast, effective and simple way of incorporating viscosity modifiers into their agrochemical formulations.

Other components of agrochemical compositions, such as non-ionic surfactants, crop oil concentrates and silicon superwetters, while possibly improving the efficacy of the herbicide solutions to which they are added, actually increase the drift risk of the spray cloud thus produced because they lower the dynamic surface tension of the spray liquid. This extends the “spray sheet” expressed from the nozzle, which breaks up further from the nozzle, thereby producing many more fine droplets.

In addition, traditional spray oils and crop oil concentrates can have a negative impact on the performance of special drift reducing nozzles (e.g. air inclusion or air induction nozzles) that are being increasingly used. These special drift reducing nozzles produce larger droplets with entrained air bubbles, which act as cushions when the large droplets strike their target, thereby reducing droplet rebound. It has been proposed that traditional spray oils and crop oil concentrates reduce the air entrapment in these large droplets, thereby increasing the likelihood of rebound from the leaf target, which reduces the efficacy of the active.

Based on the described market demands - good efficacy but limited drift – there is a need for formulations to be developed that can reduce drift without negatively affecting the biological performance of the formulations.

Reference to any prior art in the specification is not, and should not be taken as, an acknowledgment or any form of suggestion that this prior art forms part of the common general knowledge in Australia or any other jurisdiction or that this prior art could reasonably be expected to be ascertained, understood and regarded as relevant by a person skilled in the art.

Summary of the invention

The present inventors have surprisingly found that, by including significant amounts of oil in a formulation containing an agent that modifies the viscosity of a sprayable liquid containing the formulation, a concentrate can be obtained that significantly reduces the drift of a sprayed liquid containing the oil-based concentrate during spray application, reduces or prevents the undesirable agglomeration of the agent, and maintains, or even improves, the efficacy of agriculturally-active compounds applied with the formulation.

As used herein, “a viscosity-modifying agent” is not intended to encompass or include one or more agents commonly used as thickeners. The term “viscosity-modifying agent” is intended to refer to an agent that modifies (e.g. increases) the viscosity of a tank mixture or sprayable liquid to which the viscosity-modifying agent is added. It is not intended to refer to, or to include, an agent that affects the rheology of the oil-based liquid concentrate itself. This is discussed in more detail below.

The present invention relates to an oil-based liquid concentrate comprising:

- about 0.01 to about 15% w/w of an agent that modifies the viscosity of a sprayable liquid containing the oil-based liquid concentrate; and

- 56 to about 75% w/w of oil selected from vegetable, paraffin, mineral and synthetic oil, and mixtures thereof.

In one embodiment, the viscosity-modifying agent is present in the concentrate in an amount of about 0.5 to about 10% w/w. In another embodiment, the viscosity-modifying agent is present in the concentrate in an amount of about 0.5 to about 5% w/w. Preferably, the amount of the viscosity-modifying agent in the concentrate is about 5% w/w.

In a preferred embodiment, the viscosity-modifying agent is an organic polymer. The organic polymer may be a polyacrylamide, a polyethylene oxide, a poly(vinyl pyrrolidone) or a guar gum and/or its derivatives (and mixtures thereof). Preferably, the viscosity-modifying agent is a guar gum selected from the group consisting of non-derivatized guar gum, non-cationic derivatized guar gum, cationic guar gum, and mixtures thereof.

In one embodiment, the oil is present in an amount of 56 to about 65% w/w. In another embodiment, the oil is present in an amount of 56 to about 60% w/w. Preferably, the amount of oil in the concentrate is about 60% w/w (e.g. 58% w/w).

The oil may be a mixture of a vegetable oil and a paraffin or mineral oil. Preferably, the weight ratio of vegetable to paraffin or mineral oil in the oil mixture is about 1:2.

The oil-based liquid concentrate of the present invention may also comprise a dispersing agent.

Accordingly, the present invention also relates to an oil-based liquid concentrate comprising:

- about 0.01 to about 15% w/w of an agent that modifies the viscosity of a sprayable liquid containing the oil-based liquid concentrate;

- 56 to about 75% w/w of oil selected from vegetable, paraffin, mineral and synthetic oil, and mixtures thereof; and

- about 1 to about 5% w/w of a dispersing agent.

In one embodiment, the dispersing agent is present in the concentrate in an amount of about 2% w/w.

In one embodiment, the oil-based liquid concentrate consists of:

- about 0.01 to about 15% w/w of an agent that modifies the viscosity of a sprayable liquid containing the oil-based liquid concentrate; and

- 56 to about 75% w/w of oil selected from vegetable, paraffin, mineral and synthetic oil, or mixtures thereof.

The oil-based liquid concentrate may also consist of:

- about 0.01 to about 15% w/w of an agent that modifies the viscosity of a sprayable liquid containing the oil-based liquid concentrate;

- 56 to about 75% w/w of oil selected from vegetable, paraffin, mineral and synthetic oil, or mixtures thereof; and

- about 1 to about 5% w/w of a dispersing agent

In another embodiment, the oil-based liquid concentrate consists essentially of:

- about 0.01 to about 15% w/w of an agent that modifies the viscosity of a sprayable liquid containing the oil-based liquid concentrate; and

- 56 to about 75% w/w of an oil selected from vegetable, paraffin, mineral and synthetic oil, or mixtures thereof.

The oil-based liquid concentrate may also consist essentially of:

- about 0.01 to about 15% w/w of an agent that modifies the viscosity of a sprayable liquid containing the oil-based liquid concentrate;

- 56 to about 75% w/w of an oil selected from vegetable, paraffin, mineral and synthetic oil, or mixtures thereof; and

- about 1 to about 5% w/w of a dispersing agent.

In another embodiment, the oil-based liquid concentrate further comprises one or more additional agents selected from surfactants, emulsifiers, pH stabilisers or acidifying agents, wetting/spreading agents, and mixtures thereof.

The surfactant may be ionic, nonionic, amphoteric or zwitterionic, or a mixture thereof. In one embodiment, the surfactant is present in the formulation in an amount of about 20 to about 40% w/w (e.g. about 37% w/w).

In one embodiment, the surfactant is a mixture of one or more nonionic, one or more ionic and one or more amphoteric surfactants. In this embodiment, the ionic surfactants are present in an amount of about 1 to about 5% w/w (e.g. about 3% w/w), the amphoteric surfactants are present in an amount of about 10 to about 30% w/w (e.g. about 20% w/w), and the nonionic surfactants are present in an amount of about 10 to about 20% w/w (e.g. about 14% w/w).

In one embodiment, the emulsifier is present in the formulation in an amount of about 5 to about 15% w/w (e.g. about 10% w/w).

In one embodiment, the pH stabiliser or acidifying agent is present in the formulation in an amount of about 0.1 to 10% w/w. The pH stabiliser may be present in an amount of about 0.1 to about 5% w/w (e.g. about 3% w/w).

In one embodiment, the wetting/spreading agent is present in the formulation in an amount of about 1 to about 10% w/w. The wetting agent may be present in an amount of about 1 to about 5% w/w (e.g. about 2% w/w).

In one embodiment, the oil-based liquid concentrate does not comprise one or more thickening agents.

The present invention also relates to a drift-reducing sprayable liquid comprising an aqueous solution, and, dispersed in the aqueous solution, an oil-based liquid concentrate comprising about 0.01 to about 15% w/w of an agent that modifies the viscosity of the sprayable liquid, 56 to about 75% w/w of oil selected from vegetable, paraffin, mineral and synthetic oil, or mixtures thereof, and about 1 to about 5% w/w of a dispersing agent, wherein the oil-based liquid concentrate is present in the aqueous solution in an amount effective to reduce the drift of the sprayable liquid.

In one embodiment, the drift-reducing sprayable liquid further comprises one or more agriculturally-active compounds. Examples of suitable agriculturally-active compounds include fungicides, bactericides, insecticides, acaricides, nematicides, molluscicides, herbicides, safeners, plant growth regulators, plant nutrients, biologicals and repellents.

The present invention also relates to use of an oil-based liquid concentrate comprising:

- about 0.01 to about 15% w/w of an agent that modifies the viscosity of a sprayable liquid containing the oil-based liquid concentrate;

- 56 to about 75% w/w of oil selected from vegetable, paraffin, mineral and synthetic oil, or mixtures thereof; and

- about 1 to about 5% w/w of a dispersing agent,

for the reduction, during spray application, of the drift of the sprayable liquid containing the oil-based liquid concentrate.

The present invention also relates to an oil-based liquid concentrate comprising:

- about 0.01 to about 15% w/w of an agent that modifies the viscosity of a sprayable liquid containing the oil-based liquid concentrate;

- 56 to about 75% w/wt of an oil selected from vegetable, paraffin, mineral and synthetic oil, or mixtures thereof; and

- about 1 to about 5% w/w of a dispersing agent,

when used for the reduction, during spray application, of the drift of a sprayable liquid containing the oil-based liquid concentrate.

In one embodiment, the sprayable liquid contains at least about 0.000001 to about 10 % v/v (e.g. about 0.00005 to about 2.5% v/v) of the oil-based liquid concentrate, based on the weight of the spray liquid. Preferably, the amount of concentrate in the sprayable liquid is about 0.25% v/v. The sprayable liquid may also contain additives.

In one embodiment, the sprayable liquid further comprises one or more agriculturally-active compounds (as discussed above).

The oil-based liquid concentrate may also contain water. In this embodiment, the liquid concentrate comprises about 0.00001 to about 1.0% w/w (e.g. about 0.00005 to about 0.5% w/w) water.

The present invention also relates to a method of making a sprayable liquid formulation for agrochemical application comprising:

- providing an oil-based liquid concentrate comprising about 0.01 to about 15% w/w of an agent that modifies the viscosity of the sprayable liquid formulation, 56 to about 75% w/w of oil selected from vegetable, paraffin, mineral and synthetic oil, or mixtures thereof, and about 1 to about 5% w/w of a dispersing agent, in an amount effective to reduce the drift of the sprayable liquid;

- providing an aqueous solution; and

- combining the oil-based liquid concentrate with the aqueous solution;

to form a drift-reducing, sprayable liquid formulation.

In one embodiment, the aqueous solution comprises one or more agriculturally-active compounds. In another embodiment, one or more agriculturally-active compounds are added to the sprayable liquid formulation following the combining step.

Further aspects of the present invention and further embodiments of the aspects described in the preceding paragraphs will become apparent from the following description, given by way of example.

Detailed description of the embodiments

The present invention relates to an oil-based liquid concentrate comprising:

- about 0.01 to about 15% w/w of an agent that modifies the viscosity of a sprayable liquid containing the oil-based liquid concentrate;

- 56 to about 75% w/w of an oil selected from vegetable, paraffin, mineral and synthetic oil, or mixtures thereof; and

- about 1 to about 5% w/w of a dispersing agent.

As mentioned above, the present inventors have found that, by including significant amounts of oil in concentrates containing viscosity-modifying agents, a liquid concentrate formulation can be obtained that significantly reduces the drift of a sprayable liquid containing the oil-based concentrate during spray application, reduces or prevents the undesirable agglomeration of the viscosity modifier when diluted to form the sprayable liquid, and maintains, or even improves, the efficacy of agriculturally-active compounds applied with the concentrate.

It has been unexpectedly found by the present inventors that a liquid concentrate, comprising an agent (such as guar gums and/or derivative(s) thereof) that modifies the viscosity of a sprayable liquid to which it is added and a substantial portion of a hydrophobic component (the oil), can be formed, and that such a concentrate is an effective viscosity modifier of a sprayable liquid to which it is added, as well as being stable over extended periods of time. This is surprising, because before the present invention, it was understood that a number of hydrophilic agents (such as guar gums) commonly used to modify the viscosity of sprayable formulations could be used as viscosity-modifying agents in solid-, granular-, dust- or powder-type formulations. However, it was also understood that these more hydrophilic agents could not be formulated in oil-based formulations because it was thought that, in those formulations, such agents would not form stable formulations. As discussed below, it is the hydration of a number of these types of agents that is responsible for their viscosity-modifying properties. Therefore, prevention of premature hydration is a desirable property of the liquid concentrate formulation. The present invention has shown for the first time that a stable liquid oil dispersion can be used as a formulation for viscosity-modifying agents, such as guar gums. As can be seen from Example 4, the liquid concentrate of the present invention can be stored for long periods of time under normal storage temperatures while still maintaining its formulation stability and activity.

One example of a viscosity-modifying agent for use in the present invention is guar, which activates (hydrates and swells) when mixed with water. Temperature and pH extremes limit this action. In the concentrate of the present invention, guar is dispersed in the oil using dispersing agents to prevent premature activation.

In addition, in the present invention, the use of thickeners can be avoided. Thickeners (such as xanthan gum, clay compounds or surfactants with viscosity-affecting phase behaviour) are used in suspension concentrates where a solid active is insoluble in the formulation diluent. The thickener prevents the active from settling by increasing the viscosity of the concentrate.

Accordingly, thickeners are used as inert ingredients that aid formulation stability (or "shelf life"). The agent used to modify the viscosity of a sprayable liquid in the concentrate of the present invention in fact reduces the viscosity of the concentrate. Thickeners are therefore different to the agents that modify the viscosity of a sprayable liquid containing the oil-based liquid concentrate that are contemplated in the present invention. The property of viscosity modification of the sprayable liquid mixture is not related to the formulation stability aspect aided by thickeners. The viscosity-modifying agent used in the concentrate of the present invention acts on the viscosity of the sprayable mixture by swelling when it comes into contact with water. By increasing the viscosity of the sprayable mixture, the viscosity-modifying agent modifies the size of the droplets of the sprayable mixture formed by a nozzle. Therefore, in one embodiment, the oil-based liquid concentrate of the present invention does not include one or more thickening agents, but does include an agent that modifies the viscosity of a sprayable liquid containing the oil-based liquid concentrate (i.e. a viscosity-modifying agent).

Once in a sprayable mixture, the normal micellisation associated with emulsions, combined with the steric hindrance action of the dispersing agents of the formulation, combine to markedly reduce the rate of hydration after an initial guar activation period.

Without wishing to be bound by any theory or mode of action, the present inventors believe that since the process of hydration is both pH and emulsifying tendency dependent, the concentrate of the present invention is particularly useful because it has been optimised so that the final viscosity produced in the sprayable tank mixture can be controlled, to a certain degree, and in this way the tendency to form fine droplets can be controlled more precisely. This is particularly the case when a guar-based product is used as the viscosity-modifying agent, which is more commercially acceptable than other viscosity-modifying agents.

In addition, the viscosity-modifying agent is more effective than expected at the low amounts of use in the sprayable liquids. For example, a standard recommended dose of guar gum for use in sprayable droplet modifier compositions is 0.6 g/L (8 oz/100 gal). In contrast, the concentrate of the present invention allows the use of only 0.25% v/v in the tank, which is equal to 0.125 g/L. This amount of viscosity modifier is five times lower than the currently recommended, standard dose of viscosity modifier for use in sprayable formulations. However, the concentrate of the present invention is more effective than the viscosity modifier compositions currently on the market.

The present inventors have found that the concentrate of the present invention reduces the percentage of droplets in the "driftable" range (less than 150 μm diameter) by up to 50% from most spray nozzles. This can be seen from Table 2, where the concentrates of the present invention have been tested against different tank mixtures and nozzles. Further, the concentrate of the present invention can be made up easily into a sprayable formulation using standard procedures, without adversely affecting the rheological properties of the resulting sprayable formulation.

Typical polymers useful as drift reduction agents (i.e. viscosity-modifying agents) include organic polymers such as the polyacrylamides, the polyethylene oxides, the poly(vinyl pyrrolidones), and guar gum and/or its derivatives, gelatine, and the like. Currently, polyacrylamides are the most commonly used drift reduction spray tank additives in agriculture. However, synthetics such as the polyacrylamides have inherent drawbacks. For example, they are usually distributed in organic carriers, which limit the dispersibility and additionally can present a volatile organic component problem for the end user. The polymers themselves are essentially non-biodegradable and, therefore, it would be highly desirable from an environmental viewpoint to reduce their usage. Furthermore, these high molecular weight synthetic polymers are extremely sensitive to shear stresses. The high shear degradation of the synthetic polymers often realizes a significant decrease in solution viscosity over time which results, in spray processing, in a lessening of the droplet-size distribution control effects.

In summary, synthetic polymers, such as the polyacrylamides, have several major characteristics that are not conducive to ease of use or reliable efficiency: difficult dispersibility, low biodegradability, and shear sensitivity.

Natural guar and its derivatives, under controlled conditions, function as excellent drift reducing agents with essentially none of the above-identified disadvantages associated with synthetic agents such as the polyacrylamide agents.

Guar gum is the refined endosperm of the legume seed of guar beans, a plant which physically resembles the soy plant. The gum is a pure food vegetable colloid recognized by the agricultural, chemical and food formulation industry for many years as having excellent film-forming and stabilizing properties.

Functionally, non-derivatized guar gum is a cold water swelling, nonionic polysaccharide which develops and maintains its properties over a wide pH range. The guar polysaccharide is a complex carbohydrate polymer composed of essentially a straight chain of mannose units with single-membered galactose branches, chemically classified as a polygalactomannan.

Guar solutions or dispersions are simply prepared by rapidly sifting dry gum into a vigorously agitated tank of water and permitting the gum to hydrate. Higher water temperatures can shorten the hydration time so long as the heating is not so prolonged or excessive as to degrade the polymer.

At concentrations used in this invention, it is believed that solutions or dispersions of guar essentially have a zero yield value i.e. they begin to flow at the slightest shear.

The nature of guar allows almost constant viscosity for a given solution concentration over the pH range of 3 to 10. Above pH 11, a lower viscosity results from the decreased ability of the gum to hydrate. The optimum hydration range occurs between pH 5 and 8. This unusual compatibility of guar over the 3 to 10 pH range is attributed to the nonionic nature of the molecule.

Etherification and esterification reactions are made on the guar hydroxyl functionalities. The C6 hydroxyl position is the most reactive position for etherification, for example, with propylene oxide, but the secondary hydroxyls are also probable sites.

Principle etherification reactions are carboxymethylation *via* monochloroacetic acid, hydroxyalkylation *via* ethylene oxide or propylene oxide, and quaternization with various quaternary amine compounds containing reactive epoxide or chloride sites. Anionic and cationic sites modify the way the guar molecule interacts with inorganic salts, hydrated cellulosic and mineral surfaces, and organic particulates.

In general, the hydroxyalkyl ethers of polygalactomannans are prepared by reacting the polygalactomannans with alkylene oxides under basic conditions. In US 3723408 and 3723409, guar flour is reacted with alkylene oxides in the presence of water and sodium hydroxide. The reaction product is then neutralized with acid, washed with an alcohol-water mixture, and is then dried and ground. In US 3483121, the polygalactomannans and the alkylene oxides are reacted

under basic conditions with small amounts of water and larger amounts of water miscible or water immiscible organic solvents.

Specific hydroxyalkylating agents include ethylene oxide, 1,2-propylene oxide, 1,2-butylene oxide, 1,2-hexylene oxide, ethylene chlorohydrin, propylene chlorohydrin and epichlorohydrin.

Hydroxypropylation increases the gum's solubility, resulting in a product that hydrates rapidly, regardless of water temperature. Hydroxyalkyl derivatives are more tolerant of the water-miscible solvents and therefore can swell in and develop viscosity in aqueous solutions containing low molecular weight organic solvents such as methanol and ethanol. Both hydroxyalkyl and carboxymethyl derivatives typically form clearer solutions than standard non-derivatized guar gum and also hydroxyalkyl derivatives resist thermal degradation better than non-derivatized guar. Hydroxypropyl guar gum is particularly useful as a flow modifier and friction reducing agent, which does not flocculate solids, and is the most preferred derivatized guar gum of this invention.

Carboxyalkyl ethers and mixed carboxyhydroxyalkyl ethers of polygalactomannans are described in US 3740388 and US 3723409, respectively. These derivatives are made by reacting the polygalactomannan with the derivatizing agents (halofatty acid and alkylene oxide) in a water-alcohol mixture followed by washing with water-alcohol mixtures.

Specific carboxyalkylating agents include chloroacetic acid, chloropropionic acid and acrylic acid.

Carboxymethylation introduces an anionic function to the polymer chain and further increases the solubility of guar gum. Carboxymethyl hydroxypropyl guar gum is exceptional in its ability to suspend undissolved solids.

Other derivatives of polygalactomannans are described in such patents as US 2461502 (cyanoethyl ethers), US 4094795 (dialkylacrylamide ethers) and US 3498912 (quaternary ammonium alkyl ethers). In the described processes, the reactions are conducted in water-organic solvent mixtures and the reaction products are washed with solvents of water solvent mixtures. Specific quaternary ammonium alkylating agents are such agents as 2,3-epoxypropyl

trimethylammonium chloride, 3-chloro-2-hydroxypropyl trimethylammonium chloride and the like.

Grafted guar derivatives may be formed by the use of grafting reactions, and these products may or may not also be derivatized using the methodologies herein described.

Other agents that can react with the hydroxyl groups of the polygalactomannans to form ether groups are, for example, alkylating agents which include: methyl chloride, methyl bromide, ethyl chloride, ethyl iodide and isopropyl chloride; aminoalkylating agents such as aminoethyl chloride, aminopropyl bromide, and *N*,*N*-dimethylaminopropyl chloride; ethylenically unsaturated group containing agents, which react through Michael addition with hydroxyl groups, such as acrylamide, methacrylamide, acrylonitrile, methacrylonitrile, acrylic acid, sodium acrylate and, in fact, any of the polymerizable monomers which contain one ethylenically unsaturated polymerizable group.

The term "derivatized guar" is meant to include any of the above described derivatized guar gum products.

Non-derivatized guar gum, derived from a nitrogen-fixing, renewable resource, is a versatile, environmentally friendly, highly biodegradable polymer. Derivatized guar gums are slightly less sensitive to biological degradation, as the molecules are less suitable as food for common organisms.

The viscosity-modifying agent of this invention, which is selected from organic polymers such as the polyacrylamides, the polyethylene oxides, the poly(vinyl pyrrolidones) and guar gum (e.g. non-derivatized guar gum, noncationic derivatized guar gum, cationic guar gum, and mixtures thereof), gelatine, and derivatives and mixtures thereof, is present in the concentrate in an amount of about 0.01 to about 15% w/w (e.g. about 0.5 to about 10% w/w). In another embodiment, the viscosity-modifying agent is present in the concentrate in an amount of about 0.5 to about 5% w/w. Preferably, the amount of the viscosity-modifying agent in the concentrate is about 5% w/w.

The derivatized guar preferably has a molecular weight of from about 50,000 g/mol to about 10,000,000 g/mol, preferably of from about 200,000 g/mol to about 5,000,000 g/mol and more preferably of from about 1,000,000 g/mol to about 5,000,000 g/mol. Examples of

derivatized guar gum suitable for use in the concentrate of the present invention include Ag-Rho DR 2000 (a hydroxypropyl guar), marketed by Rhodia.

The oil-based liquid concentrate of the present invention also contains oil selected from vegetable, paraffin, mineral and synthetic oil, or mixtures thereof. The oil is typically present in the concentrate in an amount of 56 to about 75% w/w.

As used herein, ranges (such as 1 to 10% w/w and C_{10}-C_{22}) are intended to specify and include all ranges, as well as the individual numbers within that range. For example, the range of 1 to 10% w/w includes ranges such as 1 to 2%, 3 to 5% and 2 to 7% w/w, as well as specific amounts, such as 1% w/w, 2% w/w, 3% w/w, 4% w/w, 5% w/w, 6% w/w, 7% w/w, 8% w/w, 9% w/w and 10% w/w.

As used herein, except where the context requires otherwise, the term "comprise" and variations of the term, such as "comprising", "comprises" and "comprised", are not intended to exclude further additives, components, integers or steps.

Suitable vegetable oils are generally known and commercially available. The term “vegetable oils” is to be understood as including, for example, oils from oleaginous plant species, such as soya bean oil, rapeseed oil, maize germ oil, maize kernel oil, sunflower oil, cottonseed oil, linseed oil, coconut oil, palm oil, thistle oil, walnut oil, arachis oil, olive oil or castor oil, colza oil and canola oil. Canola oil and its derivative methyl oleate, and mixtures thereof, is particularly preferred. In the case of triglycerides, esters of C_{10}-C_{22}- and C_{12}-C_{20}-fatty acids of glycerol are preferred. The C_{10}-C_{22}-fatty acid esters of glycerol are, for example, esters of unsaturated or saturated C_{12}-C_{20}-fatty acids, in particular those having an even number of carbon atoms, for example erucic acid, lauric acid, palmitic acid, and in particular C_{18}-fatty acids, such as stearic acid, oleic acid, linoleic acid or linolenic acid.

Suitable mineral oils are various commercially available distillate fractions of mineral oil (petroleum). Preference is given to mixtures of open-chain C_{14}-C_{30}-hydrocarbons, cyclic hydrocarbons (naphthenes) and aromatic hydrocarbons. The hydrocarbons can be either straight-chain or branched. Particular preference is given to mixtures having an aromatic portion of less than 8% by weight. Very particular preference is given to mixtures having an aromatic portion of less than 4% by weight.

Suitable paraffin oils are straight-chain and branched C_{14}-C_{30} hydrocarbons. Paraffin oils are also known as base oil or white oil and are commercially available, for example, as Bayol® 85 (Exxon Mobil, Machelen, Belgium), Marcol® 82 (Exxon Mobil, Machelen, Belgium), BAR 0020 (RA.M.01I S.p.A., Naples, Italy), Pionier 0032-20 (Hansen & Rosenthal KG, Hamburg, Germany) and Kristol M14 (Carless, Surrey, England).

Suitable synthetic oils are various commercially available oils that are artificially produced from chemically-modified petroleum components or other raw materials, e.g. hydrocracked/hydroisomerized semi-synthetic or synthetic base oils belonging to API Group III such as Nexbase 2002 (Neste Oil, Belgium), Poly Alpha Olefins (POAs) belonging to API Group IV, and API Group V base oils including synthetic esters.

The oil may be present in the concentrate of the present invention in an amount of 56 to about 75% w/w (e.g. 56 to about 60% w/w). Preferably, the amount of oil in the concentrate is about 60% w/w (e.g. about 58% w/w).

The oil in the concentrate may be a mixture of a vegetable oil and a paraffin or mineral oil. Preferably, when the oil is a mixture of vegetable and paraffin oil, the weight ratio of vegetable to paraffin or mineral oil in the oil mixture is about 1:2.

The dispersing agent may be present in the concentrate of the present invention in an amount of about 1 to about 5% w/w (e.g. about 2% w/w). The dispersant will be present in an amount to facilitate the separation of particles of the viscosity-modifying agent and to prevent settling or clumping thereof. Possible dispersing agents that may be included in the concentrate of the present invention are all substances of this type which can customarily be employed in agrochemical agents. Suitable dispersing agents include nonionic agents such as linear and branched alcohol alkoxylates and alkyl phenol alkoxylates, and anionic agents such as phosphate esters and derivatives of sulphonic acids. The dispersing agent may be a mixture of various dispersing agents, including mixtures of anionic and ionic agents.

The oil-based suspension concentrates according to the invention may further comprise one or more additional agents selected from surfactants, emulsifiers, pH stabilisers or acidifying agents, dispersion and/or wetting/spreading agents, and mixtures thereof. A person skilled in the art will understand that certain agents will have more than one function i.e. a surfactant may also act as an emulsifier.

Various surfactants, or mixtures of surfactants, can be present in the composition. The surfactants include anionic, nonionic, cationic, amphoteric, and zwitterionic surfactants, and mixtures thereof. Possible surfactants that may be included in the concentrate of the present invention are all substances of this type which can customarily be employed in agrochemical agents.

Suitable nonionic surfactants include polyethylene oxide-polypropylene oxide block copolymers, polyethylene glycol ethers of linear alcohols, reaction products of fatty acids with ethylene oxide and/or propylene oxide, furthermore polyvinyl alcohol, polyvinylpyrrolidone, copolymers of polyvinyl alcohol and polyvinylpyrrolidone, and copolymers of methacrylic acid and methacrylic acid esters, furthermore alkyl ethoxylates and alkylaryl ethoxylates, which can be optionally phosphated and optionally neutralized with bases (where sorbitol ethoxylates may be mentioned by way of example), and polyoxyalkylenamine derivatives are employed.

Possible anionic surfactants are all substances of this type which can customarily be employed in agrochemical agents. Alkali metal and alkaline earth metal salts of alkylsulphonic acids or alkylarylsulphonic acids are preferred.

Possible cationic surfactants are all substances of this type which can customarily be employed in agrochemical agents. Quaternary ammonium compounds (and mixtures thereof) are preferred. Quaternary ammonium compounds include nitrogen-containing surfactants in which the molecular structure includes a central nitrogen atom joined to four organic groups, where at least one organic group is a fatty chain. Examples include nitril-based quaternary compounds (such as monoalkyltrimethylammonium salts, dialkyltrimethylammonium salts and trialkyltrimethylammonium salts), ester-based compounds (such as methyldiethanolamine esterquats and triethanolamine esterquats) and ethoxylated quaternary salts (such as monoalkyl quaternary ethoxylates). It has been found by the present inventors that cationic surfactants improve the adjuvant properties of agriculturally active compounds, such as glyphosate.

Amphoteric or zwitterionic surfactants that are suitable for use in the composition according to the invention include: betaines, such as sulphobetaines (sultaines), carboxybetaines (regular betaines), phosphobetaines, preferably alkylbetaines or alkylamidobetaines; alkylamidoamphoacetates, alkylamphoacetates, and amine oxides, which are optionally poly-alkoxylated.

The surfactant will be present in the composition of the present invention in an amount effective to improve the emulsifying, dispersing, spreading, wetting or other surface tension related properties of the sprayable formulation of the present invention. In one embodiment, the surfactant is present in the concentrate in an amount of about 20 to about 40% w/w (e.g. about 37% w/w).

The surfactant may be a mixture of one or more nonionic, one or more ionic, and one or more amphoteric surfactants. In this embodiment, the ionic surfactants are present in an amount of about 1 to about 5% w/w (e.g. about 3% w/w), the amphoteric surfactants are present in an amount of about 10 to about 30% w/w (e.g. about 20% w/w), and the nonionic surfactants are present in an amount of about 10 to about 20% w/w (e.g. about 14% w/w).

Suitable emulsifiers for use in the present invention may be any emulsifier that is capable of forming a homogenous water-in-oil emulsion when added to the sprayable formulation. Preferred emulsifiers are ethoxylated alcohols and nonylphenols, reaction products of alcohols or alkylphenols with ethylene oxide and/or propylene oxide, ethoxylated arylalkylphenols, furthermore ethoxylated and propoxylated arylalkylphenols, and sulphated or phosphated arylalkyl ethoxylates or ethoxy-propoxylates, where sorbitan derivatives, such as polyethylene oxide-sorbitan fatty acid esters and sorbitan fatty acid esters, may be mentioned by way of example.

Suitable wetting/spreading agents for use in the present invention may be any hydrophilically substituted organosilicone surfactant that is capable of lowering the static surface tension of the water in the sprayable formulation. Preferred wetting/spreading agents are polysiloxanes belonging to the organosilicone class of compounds.

The wetter may, for example, be selected from:

(i) trisiloxane polyoxyethylene surfactants of the general formula:

$$Si((\text{-O-TMSi})_2M(\text{-}(CH_2)_3\text{-}(E/P)_n)$$

where TMSi stands for $(CH_3)_3Si$-, M stands for $-CH_3$, $(E/P)_n$ stands for a polyoxyethylene group $-(OCH_2CH_2)_n-R^1$ or polyoxypropylene group $-(OCH_2CH_2CH_2)_n-R^1$ or a polymer consisting of a combination of polyoxyethylene and polyoxypropylene, where n is an integer from 1 to 50, and

R^1 is -H, -OH, $-OCH_3$, $-OC(O)CH_3$, or a linear or branched alkyl or aryl group with 1 to 20 carbon atoms;

(ii) trimethylsilane polyoxyethylene surfactants of the general formula:

$$TMSi(CH_2)_m\text{-}O\text{-}(E/P)_n$$

where m is an integer from 1 to 50, and E/P, n, R^1 and TMSi have the same nomenclature as above; and

(iii) low molecular weight (<1500 a.m.u.) polymeric forms based on a substituted siloxane chain of the general formula:

$$R^1\text{-}X\text{-}[Si(R^2)_2\text{-}O]_a\text{-}Si(R^2)_2\text{-}X\text{-}R^1$$

where the X groups can be either the same or different and are either $-(E/P)_p-$ or $-Si(R^2)_2O-$ groups, p is an integer from 5 to 30, R^2 can be either the same or different and is either linear or branched alkyl or aryl group with up to 20 carbon atoms or is $(E/P)_p\text{-}R^1$ group, with the proviso that at least one of the R^2 groups is an $(E/P)_p\text{-}R^1$ group, a equals 0 or an integer from 1 to 20, and (E/P) and R^1 have the same nomenclature as above.

Preferably, the wetter is selected from the wetters defined in (i) or (ii) above. In some embodiments, the wetter is selected from the wetters defined in (i) or (ii) above, wherein n is an integer from 10 to 20, and m is an integer from 1 to 10. In other embodiments, the wetter is selected from the super wetters defined in (iii) above, wherein a equals 0 or an integer from 1 to 10, and p is an integer from 10 to 20.

Suitable wetters include, for example, ethoxylated heptamethyltrisiloxane, polyethoxylated trisiloxane and ethoxylated polydimethylsiloxane.

Preferred acidifying agents or pH stabilisers are anionic phosphates (e.g. polyethylene tridecyl ether phosphate). Preferably, the acidifying agent or the pH stabiliser is present in the formulation in an amount of about 0.1 to about 10% w/w. The pH stabiliser may be present in an amount of about 0.1 to about 5% w/w (e.g. about 3% w/w).

The concentrate of the present invention may also include one or more additives, such as antileaching agents, rheology modifiers (such as glycol and ethylene glycol), humectants (e.g.

glycerine or glycol), fluid fertilizers, solvents, chelators (such as citric acid and EDTA), water conditioners (such as inorganic salts like ammonium sulphate, ammonium phosphate and urea, and/or acrylates and methacrylates polymers), antifoam substances, preservatives, antioxidants, colourants and inert filling materials. The additives are all substances which can customarily be employed in agrochemical agents for this purpose.

Suitable antifoam substances include silicone oils and magnesium stearate.

Possible preservatives include Preventol® (Lanxess®) and Proxel®.

Suitable antioxidants include butylhydroxytoluene.

Possible colourants include titanium dioxide, carbon black, zinc oxide and blue pigments, and Permanent Red FGR.

Suitable inert filling materials (which do not function as thickening agents) include inorganic particles, such as carbonates, silicates and oxides and also organic substances, such as urea-formaldehyde condensates. Kaolin, rutile, silica ("highly disperse silicic acid"), silica gels, natural and synthetic silicates, and talc may be mentioned by way of example.

As mentioned previously, the oil-based concentrates of the present invention also exhibit improved biological activity (see Example 5). Without wishing to be bound by any theory or mode of action, the inventors believe that the adjuvancy arises though a number of modes of action, namely:

- enhanced viscoelasticity of the droplets, thereby reducing rebound;
- the oil softening the plant cuticle, allowing more facile passage of the herbicide active through this barrier;
- maintenance of the droplet in a liquid state for longer, enhancing the mobility of the active within the droplet allowing greater chance of contact with the leaf surface; and
- larger droplets creating a concentration gradient as a driving force for penetration of the agriculturally-active compound through the cuticle of the leaf.

With regard to the "rebound" factor, it has been mentioned above that traditional spray oils and oil concentrates reduce the air entrapment in the large droplets produced by special drift reducing nozzles, thereby increasing the likelihood of rebound from the leaf target, which reduces the efficacy of any agricultural actives contained in the sprayed formulations. Without wishing to be bound by any theory or mode of action, the inventors believe that the concentrate of the present invention, when added to sprayable formulations, overcomes this deficiency either through retaining the ability of the anti-drift nozzles to entrap air bubbles or by imparting a shock-absorbing property to the spray droplets, which prevents rebound and, accordingly, prevents loss of active from the leaf.

The oil-based suspension concentrates used according to the invention may be prepared in such a manner that the components are mixed with one another in the desired ratios. The components may be combined in a preferred order such that the components are added one by one and finally the viscosity-modifying agent is added slowly to the mixture while blending/mixing is in progress. The resulting concentrate is a stable formulation.

The solid components (in particular the viscosity-modifying agent) are expediently employed in the finely ground state. However, it is also possible to subject the suspension which is formed after combining the components to fine milling or homogenising through a 35 μm stator. Preferred suspension concentrates are those in which the solid particles have a mean particle size of less than 20 μm (e.g. between 1 and 10 μm).

The oil-based suspension concentrates used according to the invention take the form of formulations that remain stable even following prolonged storage since no deposition of the viscosity modifier is observed. They can be converted into homogeneous sprayable mixtures by dilution with water. These sprayable mixtures are applied to the desired area by spraying.

Accordingly, the present invention also relates to a drift-reducing sprayable liquid comprising an aqueous solution, and, dispersed in the aqueous solution, an oil-based liquid concentrate comprising about 0.01 to about 15% w/w of an agent that modifies the viscosity of the sprayable liquid, 56 to about 75% w/w of oil selected from vegetable, paraffin, mineral and synthetic oil, or mixtures thereof, and about 1 to about 5% w/w of a dispersing agent, in an amount effective to reduce the drift of the sprayable liquid.

The present invention also relates to use of an oil-based liquid concentrate comprising:

- about 0.01 to about 15% w/w of an agent that modifies the viscosity of a sprayable liquid containing the oil-based liquid concentrate;

- 56 to about 75% w/w of oil selected from vegetable, paraffin, mineral and synthetic oil, or mixtures thereof; and

- about 1 to about 5% w/w of a dispersing agent,

for the reduction, during spray application, of the drift of the sprayable liquid containing the oil-based liquid concentrate.

In one embodiment, the sprayable liquid contains at least about 0.000001 to about 10 % vw/v (e.g. about 0.00005 to about 2.5% v/v) of the oil-based liquid concentrate, based on the weight of the sprayable liquid. Preferably, the amount of concentrate in the sprayable liquid is about 0.25% v/v. The sprayable liquid may also contain additives (as discussed above).

In one embodiment, the drift-reducing sprayable liquid further comprises one or more agriculturally-active compounds.

By “agriculturally-active” is meant a compound having an effect on plant growth, whether by killing undesired organisms or avoiding development thereof, or by directly having an effect on the plant. Examples of suitable agriculturally-active compounds include fungicides, bactericides, insecticides, acaricides, nematicides, molluscicides, herbicides, safeners, plant growth regulators, plant nutrients, fertilizing agents, biologicals and repellents. In another embodiment, the agriculturally-active compound is combined with the oil-based liquid concentrate during manufacture of a sprayable liquid.

Examples of active ingredients include: insecticides, for example carbamates, such as methomyl, carbaryl, carbofuran, or aldicarb; organo thiophosphates such as EPN, isofenphos, isoxathion, chlorpyrifos, or chlormephos; organo phosphates such as terbufos, monocrotophos, or terachlorvinphos; perchlorinated organics such as methoxychlor; synthetic pyrethroids such as fenvalerate, abamectin and emamectin benzoate; neonicotinoides such as thiamethoxam or imidacloprid; pyrethroids such as lambda-cyhalothrin, cypermethrin or bifenthrin; and oxadiazines such as indoxacarb, imidachlopryd and fipronil; nematicide carbamates, such as oxamyl; herbicides, for example triazines such as metribuzin, hexaxinone, or atrazine; sulphonylureas such as 2-chloro-*N*-[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)aminocarbonyl]-

benzene-sulphonamide; uracils (pyrimidines) such as lenacil, bromacil, or terbacil; ureas such as linuron, diuron, siduron, or neburon; acetanilides such as alachlor, or metolachlor; thiocarbamates such as benthiocarb (SATURN) or triallate; oxadiazolones such as oxadiazon; phenoxyacetic acids such as 2,4-D; diphenyl ethers such as fluazifopbutyl, acifluorfen, bifenox, or oxyfluorfen; dinitro anilines such as trifluralin; glycine phosphonates such as glyphosate salts and esters; dihalobenzonitriles such as bromoxynil, or ioxynil; dipyridiliums such as paraquat; dims such as chlethodim; fops such as fluazifop; fungicides, for example nitrilo oximes such as cymoxanil (curzate); imidazoles such as benomyl, carbendazim, or thiophanate-methyl; triazoles such as triadimefon; sulphenamides such as captan; dithio-carbamates such as maneb, mancozeb, or thiram; chloronated aromatics such as chloroneb; dichloro anilines such as iprodione, strobilurins such as kresoxim-methyl, trifloxystrobin or azoxystrobin; chlorothalonil; copper salts such as copper oxychloride; sulphur; phenylamides and derivatives such as metalaxyl or mefenoxam; aphicides, for example carbamates, such as pirimicarb; miticides, for example propynyl sulphites such as propargite; triazapentadienes such as amitraz; chlorinated aromatics such as chlorobenzilate or tetradifan; dinitrophenols such as binapacryl; foliar fertilizers that provide, for example nitrogen, potassium, phosphorus micronutrients, and other elements necessary for plant growth; and mixtures thereof.

The sprayable liquid, preferably the sprayable liquid comprising an agriculturally-active ingredient, can be ground sprayed, aerially sprayed or discharged in droplets. This is advantageously performed through an appropriate nozzle.

The application rate of the oil-based concentrates used according to the invention can be varied within a substantial range. This depends on the agriculturally-active substances in question and on their content in the concentrates and/or in the sprayable liquids.

The present invention also relates to a method of making a sprayable liquid formulation for agrochemical application comprising:

- providing an oil-based liquid concentrate comprising about 0.01 to about 15% w/w of an agent that modifies the viscosity of the sprayable liquid formulation, 56 to about 75% w/w of oil selected from vegetable, paraffin, mineral and synthetic oil, or mixtures thereof, and about 1 to about 5% w/w of a dispersing agent, in an amount effective to reduce the drift of the sprayable liquid formulation;

- providing an aqueous solution; and

- combining the oil-based liquid concentrate with the aqueous solution;

to form a drift-reducing, sprayable liquid formulation.

The aqueous solution may comprise one or more agriculturally-active compounds. Alternatively, the agriculturally-active compound(s) may be added to the sprayable liquid formulation after the combining step.

The sprayable liquid formulations of the present invention will be prepared in such a manner that the concentrate and the aqueous solution are mixed with one another in the desired ratios. For example:

1. Fill the spray tank with water to two thirds of the required amount and start agitation;
2. Add recommended amount of anti-drift formulation and mix the content well;
3. Add desired agriculturally active compounds such as herbicides/insecticides and other actives or additives according to correct mixing order and mix thoroughly; and
4. Top up the tank to desired capacity with water.

With the aid of the oil-based liquid concentrates used according to the invention, it is possible to apply agriculturally-active substances in a particularly advantageous manner to plants and/or their environment.

The concentrates of the present invention can be used to treat all plants and plant parts. In the present context, plants are understood as meaning all plants and plant populations, such as desired and undesired wild plants or crop plants (including naturally occurring crop plants). Crop plants can take the form of plants which can be obtained by conventional breeding and optimization methods or by biotechnological and recombinant methods or by mixtures of these methods, including the transgenic plants and including the plant varieties capable or not of being protected by Plant Breeders' Rights. Plant parts are understood as meaning all aerial and subterranean parts and organs of the plants such as shoot, leaf, flower and root. Examples that may be mentioned include leaves, needles, stalks, stems, flowers, fruiting bodies, fruits and seeds, and also roots, tubers and rhizomes. The plant parts also include harvested material and

vegetative and generative propagation material, for example cuttings, tubers, rhizomes, slips and seeds.

The concentrates of the present invention can be used on cereal plants such as, for example, wheat, oats, barley, spelt, triticale and rye, but also in maize, millet and sorghum, rice, sugarcane, soybeans, sunflowers, potatoes, cotton, oilseed rape, canola, tobacco, sugar beet, fodder beet, asparagus, hops and fruit plants comprising pome fruit such as, for example, apples and pears, stone fruit such as, for example, peaches, nectarines, cherries, plums and apricots, citrus fruits such as, for example, oranges, grapefruits, limes, lemons, cumquats, tangerines and satsumas, nuts such as, for example, pistachios, almonds, walnuts and pecan nuts, tropical fruits such as, for example, mango, papaya, pineapple, dates and bananas, and grapes, and vegetables comprising leafy vegetables such as, for example, endives, corn salad, Florence fennel, lettuce, cos lettuce, Swiss chard, spinach and chicory, cabbages such as, for example, cauliflower, broccoli, Chinese leaves, borecole curly kale, feathered cabbage, kohlrabi, brussels sprouts, red cabbage, white cabbage and savoy cabbage, fruit vegetables such as, for example, aubergines, cucumbers, capsicums, table pumpkins, tomatoes, courgettes and sweet corn, root vegetables such as, for example, celeriac, early turnips, carrots, including yellow cultivars, radish, including small radish, beetroot, scorzonera and celery, pulses such as, for example, beans and peas, and bulb vegetables such as, for example, leeks and table onions.

The treatment according to the invention of the plants and plant parts with the formulations used according to the invention is carried out directly or by acting on their environment, habitat or storage area in accordance with the customary treatment methods by spraying on and, in the case of propagation materials, in particular in the case of seeds, furthermore by applying one or more coats.

It will be understood that the invention disclosed and defined in this specification extends to all alternative combinations of two or more of the individual features mentioned or evident from the text. All of these different combinations constitute various alternative aspects of the invention.

The examples that follow are intended to illustrate but in no way limit the present invention.

Examples

Example 1

An oil-based liquid concentrate was prepared, which contained the ingredients shown in Table 1.

Table 1. Example ingredient list for oil-based liquid concentrate

	% mass	CAS number	Description	Purpose
	38	64742-56-9	Base oil - paraffinic	(non agrochemical) Active oil/ carrier/
	20	73891-99-3	Methyl canolate	Co active/ carrier/
	2	134180-76-0	Polyether siloxane	Non ionic, organo silicone wetter/ spreader
	3	9046-01-9	Polyethlene tridecyl ether phosphate	Anionic surfactant/ emulsifier/ pH stabiliser
	2	9038-95-3	Polyoxyalkylene Glycol Butyl Ether (alcohol polyglycol ether) EO/PO block polymer	Non ionic surfactant and dispersing agent (Plus emulsifier and wetter)
	10	68439-49-6	Alcohol ethoxylate	Emulsifier/wetting agent
	20	n/a	Blend of ammonium quaternary compound	Blended surfactant/ activator
	5	n/a	Carbohydrate polymer (Hydroxy propyl guar)	Viscosity modifier
Total	**100**			

The concentrate of Table 1 was prepared as follows:

1. The required amount of paraffinic oil was added to a suitable vessel and the mechanical blender started.
2. The vegetable oil was added followed by the nonionic dispersant, organo-silicone wetter and anionic surfactant, one after the other, while blending continued.
3. One half of the alcohol emulsifier was then added, followed by the slow addition of the entire amount of blended emulsifier with continuous mixing.

4. The balance amount of alcohol emulsifier was added and blended until a clear, transparent mixture formed.

5. Finally the guar was added slowly to the mixture and thoroughly blended until a uniform translucent liquid formed.

Example 2

The concentrate of Example 1 was diluted to a sprayable dispersion as follows:

1 Two-thirds of the required amount of water was added to a spray tank and agitation started.

2 The recommended amount of anti-drift formulation was added and the contents mixed well.

3 The desired agriculturally active compounds, such as herbicides/insecticides, and other actives or additives were added next according to their correct mixing order and mixed thoroughly.

4 The spray tank was topped up to the desired level with water.

Example 3

The formulation formed in Example 2 was tested using commonly-used herbicides and a range of hydraulic nozzles to determine the droplet size distribution at a pesticide wind tunnel research facility.

Fourteen tank mixtures comprising Roundup CT (glyphosate), Roundup DST (double salt), Surpass 300 (2,4-D) and water were sprayed through the following nozzles at designated pressures: TTI-110-02, 3 bar; AITTJ60-110-02, 3 and 5 bar; AIXR-11002, 2 bar; MD 11002, 2 bar; and Agrotop AM 110015, 2 bar. A horizontal air speed of 18 km/h was applied across the nozzles during the testing while a compressed air cylinder with pressure regulator was used to set the nozzle pressure and monitored by a calibrated pressure gauge placed close to the nozzle.

Droplet size was measured using a Sympatec HELOS VARIO Helios laser-diffraction particle-size analyser (Sympatec GmbH, Germany) with R7 lens (0.5 – 3500 µm Dynamic Size Range) 150 mm away from the nozzle to ensure full break-up of the spray sheet. Two gantries

were used to independently position the laser and the nozzle system and allow the emitted spray to be traversed through the laser beam so that the entire spray plume was measured.

Droplet sizes, droplet size range and % volume of droplets smaller than 150 μm were measured and the results statistically analysed.

Table 2 shows the driftable fines (diameter <150μm) and Table 3 the droplet size at which 10% of the spray volume is smaller ($DV_{0.1}$) and the droplet size at which 50% of the spray volume is smaller (volume median diameter, VMD) produced by each nozzle by the various herbicide/drift reducing formulation combinations in comparison to a commercially available drift reducing competitor product, LI 700 (350 g/L soyal phospholipids and 350 g/L propionic acid as marketed by Nufarm Australia Ltd).

In the tables given in this specification, “na” and “n/a” refer to combinations that were not trialled.

Table 2: Percent spray volume in droplets smaller than 150 microns.

Tank mixture	TT	TTI	TTJ	AITTJ	AIXR	MD	AM
RU CT	10	1	13	7	15	3	4
RU CT + DS 0.25%	8	1	8	4	12	2	3
RU CT + DS 0.5%	3	0	5	3	6	1	1
RU CT + LI 700	12	1	16	12	11	2	2
RU DST	16	1	16	8	15	n/a	n/a
RU DST + DS 0.25%	9	1	10	9	14	n/a	n/a
RU DST + DS 0.5%	7	0	6	4	7	n/a	n/a
RU DST + LI 700	11	1	17	12	8	n/a	n/a
RU CT + SP 300	10	1	15	9	17	3	4
RU CT + SP 300 + DS 0.25%	5	1	7	9	12	3	3
RU CT + SP 300 + DS 0.5%	4	1	7	3	11	1	2
RU CT + SP 300 + LI 700	n/a	n/a	n/a	n/a	n/a	3	3
RU DST + SP	18	1	14	9	15	n/a	n/a
RU DST + SP + DS 0.25%	10	1	10	7	12	n/a	n/a
RU DST + SP + DS 0.5%	6	0	6	4	9	n/a	n/a
RU DST + SP + LI 700	n/a	n/a	n/a	n/a	n/a	n/a	n/a

RU CT = Roundup CT @ 450 g/L = 1200 ml/50L water; RU DST = Roundup DST (dual salt) @ 1000 ml/50L water; SP = Surpass (2,4-D) @ 300 g/L = 1000 ml/50L water; DS = Drift reduction formulation @ 0.25% and 0.5% v/v.

Table 3: $DV_{0.1}$ and $DV_{0.5}$ (VMD) of spray mixtures sprayed through various nozzles in the wind tunnel.

Tank mixture	TT		TTI		TTJ		AITTJ		AIXR		MD		AM	
	$DV_{0.1}$	VMD	$DV_{0.1}$	VMD	$DV_{0.1}$	VMD	$DV_{0.1}$	VMD	$DV_{0.1}$	VMD	$DV_{0.1}$	VMD	$DV_{0.1}$	VMD
RU CT	149	332	332	731	134	308	172	392	125	296	250	473	245	495
RU CT + DS 0.25%	165	346	399	804	164	361	210	446	139	342	236	500	220	481
RU CT + DS 0.5%	243	501	455	918	193	419	229	496	184	430	323	690	247	548
RU CT + LI 700	na	na	na	na	na	na	na	na	na	na	243	474	240	490
RU DST	121	279	303	678	121	300	164	371	124	287	na	na	na	na
RU DST + DS 0.5%	175	366	421	837	185	389	217	476	173	413	na	na	na	na
RU DST + LI 700	145	295	337	646	121	248	141	303	160	311	na	na	na	na
RU CT + SP 300	148	330	329	714	124	286	157	366	115	281	229	479	218	482
RU CT + SP 300 + DS 0.25%	190	414	385	780	171	381	na	Na	135	339	253	552	222	487
RU CT + SP 300 + DS 0.5%	215	460	384	779	178	400	221	482	145	363	300	643	275	617
RU CT + SP 300 + LI 700	na	na	na	na	na	na	na	na	na	na	233	469	222	469
RU DST + SP	116	264	323	684	131	303	159	371	123	284	na	na	na	na
RU DST + SP + DS 0.5%	182	394	437	839	180	388	219	483	156	371	na	na	na	na

RU CT = Roundup CT @ 450 g/L = 1200 ml/50L water; RU DST = Roundup DST (dual salt) @ 1000 ml/50L water; SP = Surpass (2,4-D) @ 300 g/L = 1000 ml/50L water; DS = Drift reduction formulation @ 0.25% and 0.5% v/v.

Example 4

The stability of the concentrate prepared in Example 1 was tested using CIPAC standard tests recommended in the "Manual on development and use of FAO and WHO specifications for pesticides". The testing comprised accelerated storage stability (CIPAC MT 46.1.3), cold storage stability (CIPAC MT 39.1), persistent foaming (CIPAC MT 47.2) and container stability.

The results of the emulsion and dispersion test before and after hot storage are given below in Table 4.

Table 4: Emulsion Stability after Heat Storage (CIPAC MT 36.1.1 – 0.25% v/v)

Sample	**Prior to Heat storage**		**After 14 days @ 54º C** (CIPAC MT 46.1.3)	
Initial Emulsification/ dispersion	Uniform / Complete		Uniform / Complete	
Appearance	milky white		milky white	
Froth **Strike** **Emulsion Quality**	1 ml fair good and stable		1 ml fair good and stable	
Emulsion Stability (dispersion stability) (0.25%)	**Cream**	**Oil**	**Cream**	**Oil**
@ 20 min **@ 2 Hr** **@ 24 Hr**	0 ml 0ml 0 ml	0 ml 0 ml 0 ml	0 ml 0 ml 0 ml	0 ml 0 ml 0 ml
Re emulsification (re dispersion) @ 24 h	Uniform / Complete		Uniform / Complete	
Separation/ sediments	**Cream**	**Oil**	**Cream**	**Oil**
@ 24.5 hr	0 ml	0 ml	0 ml	0 ml

The testing showed that the formulation was stable under hot and cold storage conditions.

Example 5

The efficacy of the formulation of Example 2 as an adjuvant was tested with glyphosate and glyphosate plus 2,4-D herbicides against a range of commonly occurring weeds in several replicated small plot field trials in fallow situations in southern and northern regions of eastern Australia.

The treatments were applied using a 2 metre wide hand held gas operated boom incorporating four of the specified nozzles. At an application speed of 1.75 metres/second and pressures ranging from 200 to 500 kPa depending on nozzle type, treatments were applied in volumes of from 50 to 65 L/ha.

Assessments for weed control were made at 21 or 29 days after treatment (DAT) in the northern trials and 15 DAT in the southern trials by visually estimating the percentage biomass reduction. Control was rated using a 0 – 100 scale where 0 = no effect, 50 = 50% reduction in biomass and 100 = 100% reduction in biomass, compared to that in the untreated plots. Results are presented as mean percent control.

Statistical analyses were conducted using GenStat Release 11.1 (PC/Windows 2008 – Lawes Agricultural Trust, Rothamsted Experimental Station). A one-way ANOVA model was used and included all treatment effects. The data was analysed using analysis of variance and least significant difference (LSD) techniques. Means flanked by a common letter are statistically similar at the 95% level of significance.

The results of the trials are given below in Tables 5 to 9.

In summary, the addition of the formulation of Example 2 at 0.25% v/v to ROUNDUP CT increased the control of all weed species in both the southern and northern trials (Table 5 and 8) regardless of nozzle type used and despite increasing droplet VMD (Table 3).

Further, the addition of the formulation of Example 2 at 0.25% v/v to ROUNDUP CT + 2,4-D (Tables 6, 7 and 9) either increased or did not negatively affect control of all weed species in both the southern and northern trials regardless of nozzle type used and despite increasing droplet VMD (Table 3).

Table 5. The efficacy (% reduction in weed biomass, 29 DAT) of Glyphosate CT (GCT) applied at 800 ml/ha* with and without drift reducing formulation (DS @ 0.25% v/v) in small plot field trials in northern Australia

Nozzle	Description	Capeweed (*Arctotheca calendula)* (2-6 leaf)		Saffron Thistle (*Carthamus lanatus)* (2-4 leaf)		Burr Medic (*Medicargo polymorpha)* (2-6 leaf)		Flaxleaf Fleabane (*Conyza bonariensis)* (4-14 leaf, up to 15cm rosette)		Wild Oats *(Avena fatua)* (tillering to jointing)	
		GCT	GCT + DS	GCT	GCT + DS	GCT	GCT + DS	GCT	GCT + DS	GCT	GCT + DS
TT 11002	Turbo teejet	56.7	90!	23.3	51.7!	38.3	75!	na	na	na	na
TTI 11002	Turbo teejet induction	71.7	90!	40	61.7!	58.3	75	na	na	na	na
AIXR 11002	Air induction extended range	78.3	86.7	40	48.3	51.7	68.3	na	na	na	na
MD02110	Mini drift	75	85	20	40!	43.3	61.7	na	na	na	na
AM110015	Air mix	na	na	na	na	na	na	40	67!	97.5	96.3

*1000ml/ha against Fleabane and Wild Oats

! indicates significant difference between adjacent means ($P<0.05$)

Table 6. The efficacy (% reduction in weed biomass, 21 DAT) of Roundup CT (GCT) applied at 800 ml/ha with Surpass 475 (SP) applied at 415 ml/ha, with and without drift reducing formulation (DS @ 05% v/v) in small plot field trials in northern Australia

Nozzle	Description	Pigweed (*Portulaca oleracea)* (Emergence to 10 cm rosette)		Awnless Barnyrard Grass (*Echinochloa colona)* (Emergence to tillering)		Windmill Grass (*Chloris truncata*) (Emergence to tillering)	
		GCT + SP	GCT + SP + DS	GCT + SP	GCT + SP + DS	GCT + SP	GCT + SP + DS
TT 11002	Turbo teejet	69.9	94.9!	46.4	73^!	58.2	81.6#
AIXR 11002	Air induction extended range	79.9	93.2	4081.4	83.0#	83.2	89.9#
TTJ6011002	Turbo twinjet	51.9	88.2!	30	58	59.9	76.6^
AITTJ60 1102	Air-induction turbo twin jet	79.9	94.9	49.7	69.7	59.9	78.2

! indicates significant difference between adjacent means (P<0.05)

^ DS rate used was 0.25% v/v

DS

Table 7. The efficacy (% reduction in weed biomass, 29 DAT) of Glyphosate CT (GCT), applied at 800 ml/ha* with Surpass 475 (SP) applied at 415 ml/ha, with and without drift reducing formulation (DS @ 0.25% v/v) in small plot field trials in northern Australia

Nozzle	Description	Capeweed (*Arctotheca calendula)* (2-6 leaf)		Saffron Thistle (*Carthamus lanatus)* (2-4 leaf)		Burr Medic (*Medicargo polymorpha)* (2-6 leaf)		Flaxleaf Fleabane (*Conyza bonariensis)* (4-14 leaf, up to 15 cm rosette)		Wild Oats *(Avena fatua)* (tillering to jointing)	
		GCT + SP	GCT + SP+ DS	GCT + SP	GCT + SP+ DS	GCT + SP	GCT + SP + DS	GCT + SP	GCT + SP + DS	GCT + SP	GCT + SP + DS
TT 11002	Turbo teejet	68.3	80	30	36.7	56.7	80	56.7	80	56.7	80
TTI 11002	Turbo teejet induction	61.7	73.3	33.3	36.7	45	61.7	45	61.7	45	61.7
MD02110	Mini drift	85	83.3	48.3	45	78.3	76.7	78.3	76.7	78.3	76.7
AM110015	Air mix	na	na	na	na	na	na	67	67^{+}	96.3	96.3

*1000ml/ha against Fleabane and Wild Oats

+ DS used at 0.5% v/v

! indicates significant difference between adjacent means (P<0.05)

Table 8. The efficacy (% reduction in weed biomass, 15 DAT) of Glyphosate CT (GCT) applied at 800 ml/ha with and without drift reducing formulation (DS @ 0.25% v/v) in small plot field trials in southern Australia

Nozzle	Description	Annual Ryegrass (*Lolium rigidum*) Early tillering		Dense Flowered Fumitory (*Fumaria densiflora*) 4-6 leaf		Shepherd's Purse (*Capsella bursa-pastoris*) 4-6 leaf	
		GCT	GCT + DS	GCT	GCT + DS	GCT	GCT + DS
TT 11002	Turbo teejet	66.7	80!	76.7	90!	70	83.3!
TTI 11002	Turbo teejet induction	76.7	83.3!	76.7	86.7!	73.3	83.3!
AIXR 11002	Air induction extended range	70	86.7!	80	83.3	73.3	80!
MD02110	Mini drift	73.3	80!	76.7	90!	70	83.3!
AM110015	Air mix	62.5	71.3!	na	na	47.5	57.5!

! indicates significant difference between adjacent means ($P<0.05$)

Table 9. The efficacy (% reduction in weed biomass, 15 DAT) of Glyphosate CT (GCT), applied at 800 ml/ha with Surpass 475 (SP) applied at 415 ml/ha, with and without drift reducing formulation (DS @ 0.25% v/v) in small plot field trials in southern Australia

Nozzle	Description	Annual Ryegrass (*Lolium rigidum*) Early tillering		Dense Flowered Fumitory *(Fumaria densiflora)* 4-6 leaf		Shepherd's Purse *(Capsella bursa-pastoris)* 4-6 leaf	
		GCT + SP	GCT + SP + DS	GCT + SP	GCT + SP + DS	GCT + SP	GCT + SP + DS
TT 11002	Turbo teejet	80	86.7!	90	90	80	83.3
TTI 11002	Turbo teejet induction	80	86.7!	80	90!	80	86.7!
AIXR 11002	Air induction extended range	70	90!	80	90!	76.7	80
MD02110	Mini drift	80	86.7!	80	90!	80	90!
AM110015	Air mix	55	72.5!	na	na	65	69

! indicates significant difference between adjacent means (P<0.05)

CLAIMS

1. An oil-based liquid concentrate comprising:

- about 0.01 to about 15% w/w of an agent that modifies the viscosity of a sprayable liquid containing the oil-based liquid concentrate;

- 56 to about 75% w/w of oil selected from vegetable, paraffin and mineral oil, and mixtures thereof; and

- about 1 to about 5% w/w of a dispersing agent.

2. An oil-based liquid concentrate according to claim 1, wherein the viscosity-modifying agent is present in the concentrate in an amount of about 0.5 to about 10% by weight.

3. An oil-based liquid concentrate according to claim 2, wherein the viscosity-modifying agent is present in the concentrate in an amount of about 0.5 to about 5%.

4. An oil-based liquid concentrate according to claim 3, wherein the viscosity-modifying agent is present in the concentrate in an amount of about 5% by weight.

5. An oil-based liquid concentrate according to claim 4, wherein the viscosity-modifying agent is guar gum, or a derivate thereof.

6. An oil-based liquid concentrate according to any one of the preceding claims, wherein the oil is present in an amount of 56 to about 65% w/w.

7. An oil-based liquid concentrate according to claim 6, wherein the oil is present in an amount of 56 to about 60% w/w.

8. An oil-based liquid concentrate according to claim 7, wherein the amount of oil in the concentrate is about 60% w/w.

9. An oil-based liquid concentrate according to claim 8, wherein the amount of oil in the concentrate is about 58% w/w.

10. An oil-based liquid concentrate according to any one of the preceding claims, wherein the oil is a mixture of a vegetable oil and a paraffin or mineral oil.

11. An oil-based liquid concentrate according to claim 10, wherein the mixture contains a weight ratio of vegetable to paraffin oil of about 1:2.

12. An oil-based liquid concentrate according to any one of the preceding claims, wherein the dispersing agent in present in an amount of about 2% w/w.

13. An oil-based liquid concentrate according to any one of the preceding claims, wherein the liquid concentrate further comprises one or more additional agents selected from surfactants, emulsifiers, pH stabilisers or acidifying agents, wetting/spreading agents, and mixtures thereof.

14. An oil-based liquid concentrate according to claim 13, wherein the surfactant is present in the formulation in an amount of about 20 to about 40% by weight

15. An oil-based liquid concentrate according to claim 14, wherein the surfactant is present in the formulation in an amount of about 37% by weight.

16. An oil-based liquid concentrate according to any one of claims 13 to 15, wherein the surfactant is a mixture of one or more ionic, one or more amphoteric, and one or more non-ionic surfactants.

17. An oil-based liquid concentrate according to claim 16, wherein the ionic surfactants are present in an amount of about 1 to about 5% w/w, the amphoteric surfactants are present in an amount of about 10 to about 30% w/w and the non-ionic surfactants are present in an amount of about 10 to about 20% w/w.

18. An oil-based liquid concentrate according to claim 17, wherein the ionic surfactants are present in an amount of about 3% w/w, the amphoteric surfactants are present in an amount of about 20% w/w and the non-ionic surfactants are present in an amount of about 14% w/w.

19. An oil-based liquid concentrate according to any one of claims 13 to 18, wherein the emulsifier is present in the concentrate in an amount of about 5 to about 15% w/w.

20. An oil-based liquid concentrate according to claim 19, wherein the emulsifier is present in the concentrate in an amount of about 10% w/w.

21. An oil-based liquid concentrate according to any one of claims 13 to 20, wherein the pH stabiliser or acidifying agent is present in the concentrate in an amount of about 0.1 to about 10% w/w.

22. An oil-based liquid concentrate according to claim 21, wherein the pH stabiliser is present in the concentrate in an amount of about 0.1 to about 5% w/w.

23. An oil-based liquid concentrate according to claim 22, wherein the pH stabiliser is present in the concentrate in an amount of about 3% w/w.

24. An oil-based liquid concentrate according to any one of claims 13 to 23, wherein the wetting/spreading agent is present in the formulation in an amount of about 1 to about 10% w/w.

25. An oil-based liquid concentrate according to claim 24, wherein the wetting/spreading agent is present in an amount of about 1 to about 5% w/w.

26. An oil-based liquid concentrate according to claim 25, wherein the wetting/spreading agent is present in an amount of about 2% w/w.

27. An oil-based liquid concentrate according to any one of the preceding claims, wherein the oil-based liquid concentrate does not comprise one or more thickening agents.

28. A drift-reducing sprayable liquid comprising an aqueous solution, and, dispersed in the aqueous solution, an oil-based liquid concentrate comprising about 0.01 to about 15% w/w of an agent that modifies the viscosity of the sprayable liquid, 56 to about 75% w/w of oil selected from vegetable, paraffin, mineral and synthetic oil, or mixtures thereof, and about 1 to about 5% w/w of a dispersing agent, in an amount effective to reduce the drift of the sprayable liquid.

29. A drift-reducing sprayable liquid according to claim 28, wherein the oil-based liquid concentrate does not comprise one or more thickening agents.

30. Use of an oil-based liquid concentrate comprising:

- about 0.01 to about 15% w/w of an agent that modifies the viscosity of a sprayable liquid containing the oil-based liquid concentrate;

- 56 to about 75% w/w of oil selected from vegetable, paraffin, mineral or synthetic oil, or mixtures thereof; and

- about 1 to about 5% w/w of a dispersing agent,

for the reduction, during spray application, of the drift of the sprayable liquid containing the oil-based concentrate.

31. A use according to claim 30, wherein the oil-based liquid concentrate does not comprise one or more thickening agents.

32. A drift-reducing sprayable liquid according to claim 28 or 29 or a use according to claim 30 or 31, wherein the sprayable liquid contains at least about 0.000001 to about 10 % w/w of the oil-based concentrate, based on the weight of the sprayable liquid.

33. A drift-reducing sprayable liquid or a use according to claim 32, wherein the sprayable liquid contains about 0.00005 to about 2.5% v/v of the oil-based concentrate.

34. A drift-reducing sprayable liquid or a use according to claim 33, wherein the sprayable liquid contains about 0.25% v/v of the oil-based concentrate.

35. A drift-reducing sprayable liquid according to any one of claims 28, 29 or 32 to 34, or a use according to any one of claims 30 to 34, further comprising an agriculturally-active compound.