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(54) Title: A PESTICIDE, HOUSEHOLD OR INDUSTRIAL CLEANING AGENT, A PERSONAL CARE COSMETIC OR A LUBRICANT CONTAINING A SURFACTANT CONSISTING IN A BRANCHED ALKYL ALCOHOL POLYETHOXYLATED OR POLYPROPPOXYLATED, OR A SURFACTANT CONSISTING IN A BRANCHED ALKYL AMINE POLYETHOXYLATED OR POLYPROPPOXYLATED AND THEIR MIXTURES

(57) Abstract: Linear alkyl amine polyethoxylated containing in the alkyl chain 16 to 20 carbon atoms are worldwide used as surfactants for pesticides. Concerns on the negative effects on environment and health of these surfactants forced the search to new surfactants. Branched alkyl alcohols polyethoxylated or polypropoxylated as well as branched alkyl amines polyethoxylated or polypropoxylated with alkyl chains with 10-12 carbon atoms present a much lower surface tension than linear alkylamines polyethoxylated or polypropoxylated. The reason for the lower surface tension in water solutions is the steric hindrance of micelles formation caused by the branches. Micelles consisting of surfactant molecules reduce the amount of surfactant available to deposit in the interphase where they decrease the surface tension. The reason for the lower toxicity of the branched alkyl alcohol polyethoxylated or polypropoxylated as compared to linear or branched alkyl amines polyethoxylated or polypropoxylated, measured in algal growth inhibition, daphnia tests, eye irritation tests in rabbits and endocrine disruption tests, is the absence of the amine function. However, branched alkyl alcohols polyethoxylated or polypropoxylated have a limited solubility as compared to linear alkylamines polyethoxylated used before. We found that the addition of an additive to the formulation increasing the lipophilic character creates a compromise between the hydrophilic characteristics of the formulation to solve ionic or strong polar components of the formulation and the lipophilic characteristics to solve the branched alkyl alcohol polyethoxylated or polypropoxylated. There surfactants are therefore environmental friendly in the case of their application for pesticides, because they reduce the amount of pesticides per hectare and the toxicity of the spray formulation itself.



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A pesticide, household or industrial cleaning agent, a personal care cosmetic or a lubricant containing a surfactant consisting in a branched alkyl alcohol polyethoxylated or polypropoxylated, or a surfactant consisting in a branched alkyl amine polyethoxylated or polypropoxylated and their mixtures

Description

1 . Field of invention

Pesticides, Cleaning Agents, Lubricants, Environment

2 . Background of the invention

Important concerns on health and environment exist worldwide on the consequences of the application of herbicides and other pesticides for food production.

The need to strongly increase the yields of food per hectare and the quality of food are important factors influencing the use of pesticides, considering the problems of hunger.

In order to find a compromise between these two opposite factors, the European Commission approved the Regulation 1107/2009. the US Government approved FIFRA, and FAO and the World Health Organisation prepared a Manual on the Use of Pesticides adopted by all countries.

The objective is to harmonize the rules on the sales authorization of pesticides and to select for the same applications the pesticide which is more health and environment friendly.

The World Trade Organisation created a free market, and it is unacceptable that at the same time food originated in some countries is exported to other countries, where the residues of pesticides in the food do not comply with existing rules in the importing countries.

In the case of the herbicide glyphosate, we filed for two US patents with filing numbers 12 484 212, 12 691 755. These patents refer to formulations containing the surfactants branched alkyl alcohol polyethoxylated or polypropoxylated as well as the branched alkyl amines polyethoxylated or polypropoxylated.

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Preliminary tests on these formulations motivated us to enlarge the application of these surfactants also to other pesticides, cleaning agents and lubricants.

Since the pesticide glyphosate was patented by the US company Monsanto, alkylamine polyethoxylated as surfactants were included in the first patents and widely used.

Later, the length of the linear alkyl chain was subject to optimising efforts, the use of other surfactants to be mixed with alkylamine polyethoxylated was also tried, the use of other families of compounds like alkylphosphonates polyethoxylated, polysiloxanes, sarcosinates, betain polyethoxylates and many other compounds have been patented.

Glyphosate is by far the most sold pesticide worldwide, and its production volumes were even increased by the introduction in many countries of the genetic modified seeds resistant to glyphosate.

In fact, there are already in use on the agriculture market genetic modified crops which do not need fungicides or insecticides. They generate their own fungicides or insecticides.

However, genetic modified crops are not able to kill weeds, but they are able to resist to non selective herbicides, like glyphosate.

A surfactant for such large volume herbicide as glyphosate has to present a high efficacy, availability of raw materials, low toxicity and but must have a low cost.

A good surfactant allows a reduction of the quantity of active substance per hectar, and improves the speed of absorption of the water solution of the glyphosate formulation by the leaves of the weeds. This makes possible that an application of glyphosate is effective even if it rains a shorter time after application as compared to traditional formulations.

In fact, if it rains a shorter time after the application of the herbicide containing a very efficient surfactant, there will be no more herbicide on the leaves, because it was absorbed.

2 . Detailed description of the invention

It is well known from surfactant chemistry that the surfactant molecules act by making a monolayer around the particle or droplet to be dispersed or emulsified in water.

A surfactant molecule consists of a lipophilic part attracted by the particle or droplet to be emulsified and a hydrophilic part which is oriented in the opposite direction.

The surfactant orients itself on the interface water / air with the lipophilic part of the molecules oriented to the air, and the hydrophilic part directed to the center of the water drop. The surfactant builds like a fat thin layer on the water surface.

In the case of a pesticide like the herbicide glyphosate, based on this mechanism, it is possible to reduce the size of droplets when spraying a water solution on leaves of a crop.

Besides this effect, the droplets in contact to the surface of the leaves are not spherical, which would make them to fall to ground. The droplets show a large contact surface on the leaves, because the attraction of the solution molecules to the leaves is bigger than the attraction of the molecules of the solution among themselves. This larger contact surface improves the absorption speed of the active substance.

Some surfactant molecules have the tendency to come together in clusters building micelles, instead of going apart from each other and increasing the interaction with the solvent and reducing its surface tension.

The formation of micelles reduces the amount of surfactant available to reduce the surface tension.

On the other side, glyphosate is an aminoacide, therefore presenting an amphoteric character, and an isoelectric point in water solutions. The solubility of glyphosate is only 1,5% at room temperature and the pH of this solution is around 2, which is the isoelectric point.

In order to increase the solubility of glyphosate it is necessary to increase the pH by adding an alkaline hydroxide, ammonia or an amine.

It was found that the addition of an amine increases the miscibility of the surfactant in the solution.

A longer chain of the alkyl group of the surfactant normally reduces its biodegradability and increases its toxicity.

Alkyl groups contained in 2-propylheptyl alcohol polyethoxylated or polypropoxylated cause a favorable behavior in the daphnia test, in the test of

algal growth inhibition, eye irritation test, endocrine disruption and in biodegradability, as compared to linear C16 – C18 alkyl groups from natural fat. We propose now to use a surfactant consisting of branched alkyl groups as an alcohol polyethoxylated or polypropoxylated or the corresponding amine.

In order to make soluble the branched alcohol or amine polyethoxylated or polypropoxylated, we must increase the lipophilic properties of the glyphosate formulation by substituting part of the isopropylamine by an alkyl amine containing instead of 3 carbon atoms, 4 to 10 carbon atoms.

Because of its industrial availability as a raw material for plasticizers (DOP) , we used 2-ethylhexyl amine.

However, the lipophilic properties of the solution should not be too strong, in order to avoid the insolubility of glyphosate.

We must find a compromise in the mole fraction of isopropylamine to 2-ethylhexylamine in order to make soluble at the same time glyphosate and the new surfactant. We achieved that at about 1 mole ethylhexylamine to 2 - 4 moles of isopropylamine.

The formulation obtained with branched alkyl alcohol polyethoxylated or polypropoxylated is far better concerning **toxicity** than any tested alkylamine polyethoxylated or polypropoxylated , with alkyl chain branched or not.

However, the **efficacy** is similar if we use a branched alkyl amine or branched alkyl alcohol polyethoxylated or polypropoxylated.

Example

We mix following quantities in a stirred reactor with 1,5 liters:

Water	460 g
Isopropylamine	100 g
2-ethylhexylamine	65 g
2-Propylheptyl alcohol polyethoxylated	180 g

After the solution was prepared, we add

Glyphosate 95% technical grade	380 g
Total	1185 g/liter

After total solution we measured the surface tension by the ring method of a 1% water solution and found 18 mN/m. This is a better surface tension than the typical value of 32 mN/m.

Many comparative efficacy tests with rain after a short time, algal growth inhibition, daphnia, eye irritation in rabbits and endocrine disruption toxicity test were performed with very good results for our formulation.

Bibliography

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Claims

- 1 . A pesticide, household or industrial cleaning agent, a personal care cosmetic or a lubricant containing a surfactant consisting in a branched alkyl alcohol polyethoxylated or polypropoxylated, or a surfactant consisting in a branched alkyl amine polyethoxylated or polypropoxylated and their mixtures
- 2 . In the product of claim 1 where the pesticide is an herbicide consisting of a glyphosate water solution containing besides glyphosate itself, a surfactant consisting of an alkylalcohol polyethoxylated or polypropoxylated, where the alkyl group is branched in order to reduce substantially the surface tension and improve efficacy and containing both isopropylamine and an amine with 4 – 10 carbon atoms
- 3 . In the product of claim 1 where the alkyl carbon chain of the surfactant contains 10 – 14 carbon atoms, the chain is not linear and may therefore include methyl, ethyl, propyl, butyl side groups, as for example 2-propylheptyl alcohol polyethoxylated or polypropoxylated or 2-propylheptyl amine polyethoxylated or polypropoxylated.
- 4 . In the product of claim 2 where the second amine besides isopropylamine is 2-ethylhexyl amine
- 5 . In the product of claim 1 where the number of ethylene oxide or propylenoxyde monomers in the chain is 2 to 20 preferably 5 to 10
- 6 . In the product of claim 2 where the pH of the solution is adjusted to 4,2 – 5,0 in order to improve the solubility of glyphosate well out of its isoelectric point of about pH=1,5.
- 7 . In the product of claim 2 where the proportion of the C3 and C4 - C10 amines is chosen as to achieve a lipophilic – hydrophilic compromise to make soluble at the same time glyphosate and the surfactant.
- 8 . In the product of claim 1 where the branched alkyl alcohol polyethoxylated or polypropoxylated is mixed in a proportion of 1 to 99% with linear or branched alkyl amines polyethoxylated or polypropoxylated, alkylphosphonic acids polyethoxylated or polypropoxylated.