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(54) Title: TEXTILE PRODUCT FOR KILLING INSECTS

(57) Abstract: An improved textile product comprising an insecticide and at least one more different active ingredient and which kills insects and is more effective as compared to textile products, which contain only one insecticide for the killing of same insects especially in the aspect of overcoming or preventing insecticide resistance.

TEXTILE PRODUCT FOR KILLING INSECTS

FIELD OF THE INVENTION

The present invention relates to an improved textile product comprising an insecticide and at least one more different active ingredient and which kills insects and is more effective as compared to textile products, which contain only one insecticide for the killing of same insects especially in the aspect of overcoming or preventing insecticide resistance.

BACKGROUND ART

Malaria is a vector-borne infectious disease caused by protozoan parasites (genus *Plasmodium*). The most serious forms of the disease are caused by *Plasmodium falciparum* and *Plasmodium vivax*, but other related species (*Plasmodium ovale*, *Plasmodium malariae*, and sometimes *Plasmodium knowlesi*) can also infect humans. This group of human-pathogenic Plasmodium species is usually referred to as malaria parasites.

During the last decade, pyrethroid (insecticide) treated mosquito nets have become the main method for malaria prevention in many malaria - endemic African countries. Long lasting insecticidal (hereafter LLIN) nets are nets treated with insecticides at factory level where the insecticide is coated around or incorporated into the yarns. The nets typically resist multiple washes and its biological activity last as long as the net itself (2-3 years for polyester and 4-5 for polyethylene yarns). The use of bednets is a prevention tool that prevents transmission, i.e., that humans get infected with the malaria protozoan parasite and that mosquitoes pick up the parasite from infected people. The parasites develop inside the mosquitoes and will be transferred during a later blood meal 10-14 days later, if the mosquito survives so long time. If humans use a net e.g. a bednet, the mosquito contacts the insecticidal net and hereby receives a mortal dosage of insecticide. The mosquito thus dies and hereby never reaches the human and infection is prevented. An additional effect of pyrethroid is that some mosquitoes will be repelled from the net since these insecticides have contact- irritant effect. This effect may even to some degree prevent the mosquitoes to enter a room where a pyrethroid net is in use.

It is well known that insects under insecticidal pressure may develop resistance.
One of the resistance mechanisms developed against pyrethroids is the so-called knock down resistance (kdr). The gene(s) causing pyrethroid knockdown (kdr gene) has become widespread in *Anopheles gambiae* (a mosquito carrying malaria parasites) in West Africa (N'Guessan et al., Emerging infectious diseases cdc/eid volume 13 No.2). There are many literature publications available indicating the increased incidence of resistance development of malaria mosquitoes against the insecticide group of pyrethroids and more specifically Deltamethrin and Permethrin,

which are used in such LLIN, bednets. Other mechanisms than kdr can be involved e.g. oxidases. Due to increasing insecticidal resistance, the LLIN bednets are becoming less effective in the prevention of malaria. Therefore, new strategies are under development.

One suggested method is to use two insecticides with different insecticidal resistance mechanisms. This can for example be an insecticide from the group of carbamates (organophosphate group) combined with pyrethroids (e.g. Deltamethrin or Permethrin). P. Guillet et al published in March 2001 (Medical and Veterinary Entomology 15 (1), 105–112) the idea of combining a pyrethroid and a carbamate in a so-called 'two-in-one' treated mosquito net. The article describes how these two insecticides can be applied to different parts of bednets. The objectives are mainly to overcome certain limitations of pyrethroid-impregnated bednets currently recommended for malaria control purposes.

Apart from developing alternatives to pyrethroid dependency, the authors sought to counteract pyrethroid irritant effects on mosquitoes (excito-repellency) and resistance to pyrethroids. The idea takes advantage of the presumed host-seeking behaviour of mosquitoes confronted by a net draped over a bed, whereby the mosquito may explore the net from the top downwards. Thus, nets could be more effective if treated on the upper part with residual non-irritant insecticide (carbamate or organophosphate) and with a pyrethroid on the lower part. Sequential exposure to different insecticides with distinct modes of action is equivalent to the use of a mixture as a potential method of managing insecticide resistance.

The method used by the authors is a pretreatment of untreated bednets (polyester textile bednet with bifenthrin (pyrethroid group insecticide) and carbamate (organophosphate group insecticide). As the author describes, polyester bednets were pretreated with residual pyrethroid (Bifenthrin 50 mg/m^2 or Deltamethrin 25 mg/m^2) on the lower half and with carbamate (Carbosulfan 300 mg/m^2) on the upper half to minimize contact with net users. Unreplicated examples of these 'two-in-one' treated nets were field-tested against wild mosquitoes, in comparison with an untreated net and bednets treated with each insecticide alone, including PermaNet ® wash-resistant formulation of Deltamethrin 50 mg/m^2.

The outcome was that overall the best impact was achieved by the bednet treated with carbosulfan alone, followed by 'two-in-one' treatments with carbosulfan plus pyrethroid. Blood-feeding rates were 13% *An. gambiae* and 17% *Cx. quinquefasciatus* in huts with untreated nets, but only 3% with carbosulfan insecticide treated nets (ITN), 7–11% with combined. The author finally concluded that further development of this new 'two-in-one' ITN concept requires a range of investigations (choice of effective products, cost-benefit analysis, safety, etc.) leading to factory production of wash-resistant insecticidal nets treated with complementary insecticides.

In Am. J. Trop. Med. Hygiene 2005 June; 72 (6): 739-744, Pennetier et al also discusses the combination of a non-pyrethroid insecticide and a repellent as a new approach for controlling knockdown –resistant mosquitoes. In that context, the efficacy of a mixture of a repellent (N,N-diethyl toluamide [DEET]) and a non-pyrethroid insecticide (propoxur, a carbamate) was investigated under laboratory conditions against both pyrethroid-susceptible and pyrethroid-resistant mosquitoes with the knockdown resistance (kdr) mutation. The results showed that a combination of propoxur (carbamate) and DEET induced a knockdown effect and mortality as high as Deltamethrin (a standard pyrethroid) against the susceptible strain, and significantly higher efficacy against the pyrethroid-resistant strain. This could be explained mainly by the existence of a strong synergistic interaction between DEET and propoxur in mosquitoes. This study constitutes a first step towards an alternative strategy for improving mosquito control in areas with pyrethroid resistance.

In a later study, published in the Malaria Journal March 2007, 6:38, Cédric Pennetier et al, further describes the idea to use two insecticides as a strategy to combat malaria resistance specifically against pyrethroids. The authors combine one carbamate and two repellents on nets, separately or in mixture. The untreated malaria bednets (textile yarns) were brought into contact with the insecticide and/or repellents mixtures by simple dipping the textile into a solution of insecticides and/or repellents. This is a simple laboratory method and is generally known by people skilled in the art. The method of dipping leads to a net, which can be tested but is far from optimal and is often not stable in the time. The insecticide is often not well attached to the surface, is also irregular spread over the surface and could disappear within e.g. 2 days due to climate influences (rain or UV from the sun exposure) or could disappear simply by handling (putting up the net and taking it down).

Prior art patent documents published in this area are typically related to technologies using one insecticide. WO00137662 (Ole Skovmand, Intelligent Insect Control) provides an impregnated netting or fabric for killing insects by forming a substantial continuous film surrounding the insecticide/repellant together with the yarn. WO00137662 briefly mentions on page 9 to 11 starting line 15; the possibility of using two insecticides (impregnating netting, fabric) as a strategy to combat resistance development of insects. As suggested, it may be advantageous to replace the pyrethroid with another insecticide with a low mammalian toxicity or to impregnate a part of the mosquito net with a pyrethroid and a part of it with another insecticide. Such a combination may also be used in general as a strategy to delay resistance development. WO00137662 does not provide solutions, examples or data proving that such textile products can actually be released in combination and there is generally lack of data to claim such invention.

WO2007085640 (Ole Skovmand, Intelligent Insect Control) describes a textile for killing insects characterized by presence of solid insecticidal particles on the surface of the textile as a release mechanism for the chosen insecticide.

PermaNet 3.0 is manufactured by Vestergaard Frandsen (Switzerland). The product is a combination of different LN technologies and is designed for the control of insecticide resistant mosquito populations.

WHO published (8-11/12 2008) the results of permanet 3.0 and can be downloaded at: http://whqlibdoc.who.int/hq/2009/WHO_HTM_NTD_WHOPES_2009_1_eng.pdf.

The roofing of PermaNet 3.0 utilizes deltamethrin and a synergist, piperonyl butoxide, incorporated into monofilament polyethylene yarn of 100 denier (warp-knitted fabric, with weight of 40 + 15% g/m2) at the target dosage of 4.0 g AI/kg and 25 g AI/kg of netting material respectively.

The side panels of PermaNet 3.0 are made of multi-filament polyester fibres, treated with deltamethrin in a resin coating (75 + 5% denier, warp-knitted fabric, atlas construction). The side netting has two parts: a strengthened lower part, so-called border (70 cm) by using 75 + 5% denier yarn (weight 40 + 10% g/m2) and a side panel made of 75 + 5% denier (weight of 30 + 10% g/m2).

The target dosage of deltamethrin in the side panels is 2.8 g AI/kg of netting material, i.e. 115 mg AI/m2 of the border and 85 mg AI/m2 of the remaining of the side panels.

In summary, this is a textile product made of filaments or yarns (polymer composition) comprising two active ingredients; deltamethrin (1) and piperonyl butoxide (2) - named PPB herein).

However, as the efficacy research done by WHO clearly concludes, this product (filament or yarns) does not work.

As appears from the report, unwashed yarn with two active ingredients (polyethylene composition) performs better than one insecticide BUT after washing 20 times as the WHO test requires and as referred to in present application as reference 4 (page 10 , first paragraph), the difference disappears and there is no significant different kill between two active ingredients or one active ingredient. A likely explanation would be that the initial effect is due to the combined presence of deltamethrin and Piperonylbutoxide in effective ratio, but after washings, one (probably the piperonyl butoxide) or both of the ingredients do not reappear at the surface

at a sufficient concentration and optimal ratio, and the product is not better than a product with just deltamethrin.

Further on page 58 of the WHO document as referred to above, clearly concludes that PBO and deltamethrin are not released with the same rate and reads: (page 58 – third paragraph):

"The PBO retention after washing was slightly lower than that of the deltamethrin in the roof. PBO retention increases with the number of washes and after 15 washes no release of PBO seems to occur."

The WHO committee recommends and concludes: page 59 – last paragraph which states following a review of the available evidence, the meeting concluded - that the PermaNet 3.0 cannot be considered as a tool to control mosquito populations resistant to pyrethroids or to prevent the spread of pyrethroid resistance. However, the meeting commended the manufacturer for its initiative in developing tools to control pyrethroid-resistant mosquitoes and encourages it to conduct further research and development in this area.
In summary, the prior art has developed methods, yarns and finished textile products (bednets) which teach how to attach or integrate an insecticide onto or into yarns.

According to the art, this can be one insecticide and one of the same yarns used for all sides of bednets (top part, left and right side), or one can constructed as a top part of one insecticide, and a side part from yarn/textile of another insecticide and than simply sew them together.

In short, these two insecticides textile products may be seen as textile product using the SAME type of yarn – i.e. the yarn as such (without insecticide) is the same all over the textile product as such.

There are definite needs to further improve textile products and insecticide containing yarns.

SUMMARY OF THE INVENTION

The problem to be solved by the present invention is to provide an improved textile product that can be used for reducing the development of insecticide resistance and which also kills insects that have developed resistance to some of insecticides or at least sterilize those preventing insects to contribute to the development of future resistant insect populations.

The solution may be seen as the provision of a textile product, where insecticides (or insecticides and synergists) are combined and are present in fixed ratios during the lifetime of the product.

The solution as described herein is based on that the present inventor identified serious problems with the release rate for prior art known insecticide treated bednets comprising two different insecticides. In short, and as discussed herein the present inventor identified that the two different insecticides are released at different rates. As discussed herein this gives serious drawbacks with respect to development of insecticide resistance.

Current insecticide treated bednets have one or two insecticide on the surface coated or incorporated into the yarn and the formulation technology used, dictates certain controlled release of the insecticide in the time. In example 4 herein, are prepared typical products (prior art) and are examples of two insecticides incorporated into one yarn, and are released at different rates.

The insecticide needs to be released in a sufficiently high concentration to kill insects, but the insecticide also needs to be protected against i.e. UV radiation, handling and washing by the consumer and thus the insecticide needs to stick well onto the filament/yarn surface. This corporation between one insecticide and chosen chemicals to steer the release, is a fine balance and is achieved by research identifying the best composition of selected chemicals and polymers.

As it concerns the use of two insecticides in the SAME yarn – as described in the prior art - the present inventor found that the release is be out of balance.
Without being limited to theory, this is due to predictable different migration speeds of different insecticides. One insecticide will migrate faster to the surface than the other. The result is thus that one insecticide reaches the surface first and hereby the benefit of using two different insecticides is definite lost. Also, the finished textile product, long-lasting impregnated bednet, will have a different life time i.e. one part which is probably still viable killing some populations of insects and another part which is exhausted already. These products are not effective in the field and will not control resistant insect populations.

Some manufacturers are also solving this problem by for example drastically increasing the concentration of the insecticides onto or into the yarn. This results in unnecessary environmental waste and probably also safety issues (skin irritations) for the end user of the textile products and is not resulting in the control release of both chosen insecticides.

The problem can also clearly be observed in the above described article of Pennetier et al, 2005 (Am. J. Trop. Med. Hygiene 2005 June; 72 (6): 739-744). Here it is demonstrated that DEET works as a synergist for organophosphates and carbamates, and allow for use of a low concentration of these insecticides. The experiments were done using filter paper treated with the technical grade of each insecticide and repellent. Filter papers were treated following a World Health Organization (WHO) protocol using acetone solutions of insecticide and silicone oil as the carrier. The impregnation was done by dripping evenly onto the paper 2 ml of technical grade substance dissolved in acetone and silicone oil. The paper was dried for 12 hours before the test. Pennetier et al showed, however, that DEET is very volatile, and consequently the insecticidal or repellent effect has a very short life time and if this would be applied on a net, the net will only contain low concentrations of the organophosphate that will have no killing effect, not even on non-resistant insects. Clearly, though, theoretically interesting, without formulation technology suitable for textile products made which are made of polyethylene or polyolefin's in general, assuring a continuous presence of both insecticides at the right proportions, such a product suggested by Pennetier et al, would have no practical value and would not pass the testing requirements for a commercial net.

One solution of the present invention is based on incorporating one active ingredient in a filament, and another active ingredient into another filament with each its specific release composition.

Each of the filaments thus comprises an active ingredient and releases the active ingredient to the surface and both release compositions are composed in such a way and are different compositions that the release is simultaneous, over the entire life time of the textile product. The filaments are then combined e.g. by twisting after that and a yarn is made from the filaments. The yarn thickness can be for example 75, 100 and 150 dernier. This is called denier. The term "denier" herein relates to yarns, which can be extruded in different thickness. Denier is a term relating to the fineness of the yarn filament. More precisely, denier is the weight in gram of 9000 meters of yarn.

Yarns with such characteristics can be used separately (i.e. 1 insecticide in the yarn with filaments comprising only one insecticide and a second with an insecticide, a synergist or a chemosterilant) to thereafter weave or knit a textile product, tent or even cloth for killing insects.

Yarns can be monofilament yarns or polyfilament yarns. For example; a monofilament yarn with piperonyl butoxide and another monofilament yarn with bifenthrin. These two yarns can be woven together or knitted in the shape of a net, which then is composed of two different yarns with each its insecticide.

Each yarn comprises its specific insecticide and its specific release composition, which is prepared in such as way that the insecticide is controlled released according to its chemical characteristics and is approximately releasing at equal speed and ratio compared to the second insecticide or synergist.

Accordingly, a first aspect of the invention relates to a textile product to kill insects,

(1a): wherein the textile comprises at least two different yarn types characterized by that:

(i): the first yarn type releases at least one active ingredient selected from the group consisting of an insecticide and the second yarn type releases at least one active ingredient, but not the same as the first yarn, selected from the group consisting of an insecticide, an insect repellent, pesticide synergist and a chemosterilant;

or

(1b): wherein the textile comprises a yarn comprising at least two different filament types spun into the yarn characterized by that:

(i): the first filament type releases at least one active ingredient selected from the group consisting of an insecticide and the second filament type releases at least one active ingredient, but not the same as the first filament type, selected from the group consisting of an insecticide, an insect repellent, pesticide synergist and a chemosterilant;

and wherein

(a): the two different active ingredients are both present on the surface of the yarn after 20 defined laboratory washes; and

(b): the release rate of the two different active ingredients are essential the same for both, as measured by determining the slope of the decay as described in example 3 and where the slope of decay for the two different active ingredients may not be significantly different, defined as the confidence is at least 90%.

Based on the detailed instructions/descriptions herein it is routine work for the skilled person to control the active ingredients release rate of the yarns to get a release rate that is not significantly different for the different relevant active ingredients of interest.

In example 3 is provided detailed instructions on how to measure if the release rate of the two different active ingredients are essential the same – as required in point (b) of the first aspect.

Essentially the method of example 3 relates to measurement of slope of decay for the two different active ingredients. If the Confidence is at least 90% - it is believed that the release rate for the two different active ingredients is sufficient similar to solve the problem as described herein – i.e. reducing the development of insecticide resistance.

All individual measurement steps of example 3 may be considered as standard routine steps for the skilled person. Accordingly, by following example 3 it is routine work for the skilled per-

son to determine if a textile product of interest fulfills the criteria of point (b) of the first aspect.

As discussed above, the yarn can be a polyfilament yarn. In its most simple composition, it can be 2 filaments with e.g. each its different insecticide and one chooses to compose this into one yarn. One can make as such for example a yarn with 30 filaments, 15 have insecticide 1 with release composition-1 and 15 with for example piperonyl butoxide with release composition-2. To obtain a proportion of the two insecticides, one insecticide could be present in a majority of the filaments and the other in the minority rest. This polyfilament yarn is than useful to make bednets, nets, tents and protective cloths.

The invention is therefore also useful to make new yarns with specific release compositions. Once filaments are prepared with each a different insecticide, a new yarn composed of separate filaments each comprising 1 insecticide. These can than can be e.g. twisted into a new yarn with unique characteristics in terms of killing efficacy of insect populations. The new yarn thus comprises at least two filaments with each filament specific insecticide released on the surface; at least two insecticides will be present on the surface of such new yarn. The advantage is that an insect is exposed to at least two insecticides and thus the chances to be killed will significantly increase.

The availability of the herein described new yarns will give the manufacturers of insecticidal treated bednets an enormous flexibility to compose a new improved bednet, which fits the kind and specific level of resistance in endemic malaria countries and this will help to control the levels of resistant development in insects as they are continuously exposed to different groups of insecticides, each having its unique mode of action. Thus the insect under biological pressure must develop multiple resistant mechanisms, which is more difficult then developing resistance against one type of insecticide with its specific mode of action (e.g. only the kdr gene mutation).

By this invention, many different textile products are now possible to manufacturer and the products will have approximately equal life time and efficacy. Thus one may manufacture sides and parts of a yarn 1 with insecticide 1, another side with yarn 2 with insecticide 2, and a roof 3 with insecticide 3. Or, a side with yarn 1 insecticide 1 and a side part with a yarn 2 with repellant 1. Many different combinations are possible depending on the chosen strategy for resistance defense and will actually control the resistant populations by have controlled release of the at least two chosen insecticides.

The term “lifetime” is defined herein as of the life time a textile product (for example mosquito net) is of course depending on the use, but generally for a mosquito net, the maximal lifetime is 7 years. The lifetime (years) depends on the time the net is still intact (no big holes) and the

insecticide or insecticides are still present in a dosage sufficient to kill mosquitoes. World Health Organization further referred to as WHO herein, demands that bednets declared to be long lasing must last at least 3 years and preferably 5 or more years.

In summary, all these insecticides are present in sufficient dosages during the life time of the product, and when one is a synergist, in a fixed ratio to the insecticides it synergizes.

Another combination is to simply use yarns at randomly by knitting for example every 10th cm yarn 1 with insecticide 1 and the next layer of 30 cm with yarn 2 with insecticide 2. It can also be imagined to use knitting techniques where yarn 1 and yarn 2 in this example, are inter-mixed so that one hole which can be square shaped or diamond shaped depending on the knitting technique, comprises yarns on top of each other (double loop yarn), hereby achieving the benefit of release of more than one insecticide as close as possible to each other and concentrated on one place. This has the advantage that a mosquito will be exposed to two or more insecticides and synergists, and hereby a higher effective kill of the said insect can be achieved.

Accordingly, a second aspect of the invention relates to a method to manufacture a textile product of the first aspect comprising the following steps:

(Ia): making a first yarn type that release at least one active ingredient selected from the group consisting of an insecticide and a second yarn type that release at least one active ingredient, but not the same as the first yarn, selected from the group consisting of an insecticide, an insect repellent and a chemosterilant;

or

(Ib): making a yarn comprising at least two different filament types spun into the yarn characterized by that:

(i): the first filament type releases at least one active ingredient selected from the group consisting of an insecticide and the second filament type releases at least one active ingredient, but not the same as the first filament type, selected from the group consisting of an insecticide, an insect repellent and a chemosterilant;

and

(IIa): weaving or knitting parts of the textile product comprising the first type of yarn with one active ingredient and other parts with the second type of yarn comprising another different active ingredient (in case of step Ia) ;

or

(IIb) weaving or knitting the textile product by mixing the yarn types (in case of step Ia) or the yarn type (in case of step IIb) randomly in all relevant parts of the textile product;

and

(III) cut the textile product and shape it into a bednet, tarpaulin or any given shape fitting the end use.

A third aspect of the invention relates to a textile product to kill insects of the first aspect obtainable by a method of the second aspect.

DEFINITIONS

Prior to a discussion of the detailed embodiments of the invention is provided a definition of specific terms related to the main aspects of the invention.

Generally, all the definitions of the relevant terms herein should be understood as the skilled person would understand them in the present technical context.

The term "active ingredients are both present on the surface of the yarn after 20 defined laboratory washes" of the first aspect relates herein to what may be said to be a standard requirement for releasing a textile product to kill insects on the market according to the WHO guidelines. In line of this and as describing herein the washes shall be made according to WHO standard wash test guidelines as described in reference 4 herein. As known to the skilled person this wash test is performed to have an indication of the required lifetime [e.g. 3 to 7 years] of the textile product to kill insects.

The term "filament" denotes a solidified polymer, which has passed through the spinneret. When the filament dries or solidifies, it forms what is called a continuous filament yarn. The material can consist of a single polymer type, polymer mixes and its' mechanical, chemical and colors can be changed with various additives.

The term "different filament types" is defined herein as the first filament type is different from the second filament type as such in their composition without the presence of the relevant active ingredients. As understood by the skilled person based on the present description – the individual filament types will differ with respect to e.g. relevant polymers, additives and components that are used to control the release rate of the active ingredients as described herein.

The term "different yarn types" is defined herein as the first yarn type is different from the second yarn type as such in their composition without the presence of the relevant active ingredients. As understood by the skilled person based on the present description – the individual yarn types will differ with respect to e.g. relevant polymers, additives and components that are used to control the release rate of the active ingredients as described herein.

The term “yarn” denotes a long continuous string made of either a single or several filaments and is suitable for use in the production of textiles, sewing, crocheting, knitting, weaving, embroidery and rope making. A yarn can be made out of monofilaments or poly-filaments. The term “monofilament yarn” refers to a yarn that consists of only one filament. The term “polyfilament yarn” refers to yarns made from several filaments that are twisted, spun or interlocked together to form a continuous yarn.

DRAWINGS

Figure 1: Theoretical presents a graphical (linear) presentation of decay of two insecticides, each present in its yarn.

Figure 2: The linear data of figure 1, are then transformed to logarithmic and the lines than typical becomes straight decay lines which can then be statistically analyzed.

Embodiments of the present invention are described below, by way of examples only.

DETAILED DESCRIPTION OF THE INVENTION

Textile product

The textile product may be a net such as a bednet.

A roof and two sides typically characterize a bednet as an example of a textile bednet. The sides of the net are in closest contact with the humans which are sleeping or resting under the bednet and it is thus preferred that the used insecticide for the sides is a public health safe net with as few as possible human health side effects.

By using two different yarns with each its different insecticide, the different yarn types can be used to construct the bednet in such a way that the roof comprises an insecticide which has a different human toxicological profile (more toxic) than the side of the bednet (less toxic for humans). One of the problems which current technological development in this area is that only very few insecticides can be used for this unique application to kill insects mainly because of the limitations given by the toxicological profile of the insecticides. There are many approved insecticides available as pesticides used in the agricultural industry to protect crops against insect damages. However, too few are approved for public health purposes. This is also one of the reasons that pyrethroids are used in such net technology. Such insecticides must be approved for public health and undergo a special approval to quality for such use

where the approval is mostly depending on the safety profile (human toxicity and side effects) for use in the public health sector.

Thus current invention opens up the possibility to use more toxic insecticides (toxic for humans) with reduced risk of toxicity humans as these yarns containing the more toxic insecticides can be used but located in such way that the human toxicity risk is reduced. An example of this is making use of the roof part. The roof part, which is the part located most far away (for touching, skin contact, mouth contact) during the normal use of the bednet, the contact of textile with humans is minimum (only in contact during mounting the net) and therefore the use of a slightly more toxic insecticide is herein made possible.

The textile product may be in form of net, bednet, mosquito bednet, curtain, cushion, wall covering textile, tarpaulin, cloths, or window/door screen.

Insects

Malaria is described herein as the major target for the protection of humans using the herein described insect textile products in the form of bednets, roofing material or tarpaulins. The major species infective to humans are *Plasmodium falciparum* and *Plasmodium vivax*. There are specific species indigenous to continents and countries. It is understood herein that these are killed by the herein described invention. However, other vector borne diseases like denghue fever, yellow fever, leishmaniasis, filariasis, borellia and other diseases vectored or transported by invertebrates may also be targeted with such insecticide or acaricide treated textiles.

Examples of herein relevant insect species are: Anopheles spp, *gambiae, arabiensis, funestus, culifacies, stephensi, minimus, (dirus), fluviatilis, nivipes, philippinensis, sundaicus, annularis* and *varuna*. Other biting insects where the herein described textile products can be usefull to protect humans are biting insects. Generally biting insects such as; biting mosquitoes in the genus *Aedes, Anopheles* and *Culex* and phlebotomes ("sandflies") and more specific Anopheles species such as but not limited to An. gambiae, An. *funestus*, An. *stephensi* and An. *darlingi* and also *Aedes* genus and species: *albopictus* and *aegypti* and *Culex* species such as Culex *pipiens* and *quinquefasciatus*.

Different yarn types and different filament types

As discussed above, the term “two different yarn types” is defined herein as the first yarn type is different from the second yarn type as such in their composition without the presence of the

relevant active ingredients. As understood by the skilled person based on the present description – the individual yarn types will differ with respect to e.g. relevant polymers, additives and components that are used to control the release rate of the active ingredients as described herein.

As discussed above, the term "different filament types" are defined in a similar way.

As discussed above, based on the detailed instructions/descriptions herein it is routine work for the skilled person to control the active ingredients release rate of the yarns to get a release rate that s significantly different for the different relevant active ingredients of interest.

Below are described suitable examples of useful release compositions.

The term "release composition" describes a special developed composition of chemicals including the polymer composition combined in such a way that the chosen different active ingredients are released at roughly the same speed and in roughly the same ratio in the different filaments or yarns. As discussed herein, this guarantees that chosen different active ingredients have equal life time throughout the use of the textile product (e.g. a bednet)

The release compositions comprise different components depending of the function. Below are described different components with specific functions and preferred materials to obtain the preferred release characteristics.

Components C are components belonging to the group of anti-oxidants. Anti-oxidants include oxygen-radical scavengers, HALS (Hindered Amin Light Stabilizer) and NOR-HALS (Alkyloxamin Hindered Amin Light Stabilizer) molecules. Their role is to prevent destruction of the active ingredients and UV filters during processing and use, especially during weathering with UV exposure. Nickel quenchers, steric hindered phenols, phosphits, phosphonits, thio-co-stabilisers and HALS molecules are used to prevent the destruction from oxygen or combinations of oxygen, residual catalysts from the polymerization process, UV activated molecules that become electronic donors. This oxygen – radical scavengers increase stabilization of the synthetic polymer during processing as well as during use and also protect the active ingredient(s) and less stable UV filters. These products are produced by the company Ciba Geigy under trade names such as but not limited to CHIMASSORB® 81, TINUVIN 494 and IRGANOX.

CHIMASSORB® 81 is a solid-form UV absorber of the 2-hydroxy-benzophenone class imparting good light stability when used in combination with HALS of the Chimassorb or Tinuvin range. It shows good compatibility with polyolefin and plasticized PVC.

Tinuvins are belonging to the group of light Stabilizers. As they are compositions of compounds, they are composed according to their action mode: UV absorbers (UVAs) that act by shielding the polymer from ultraviolet light or hindered amine light stabilizers (HALS) that act by scavenging the radical intermediates formed in the photo-oxidation process.

Hindered Amine Light Stabilizers

Hindered Amine Light Stabilizers (HALS) are extremely efficient stabilizers against light-induced degradation of most polymers. They do not absorb UV radiation, but act to inhibit degradation of the polymer, thus extending its durability. Significant levels of stabilization are achieved at relatively low concentrations. HALS' high efficiency and longevity are due to a cyclic process wherein the HALS are regenerated rather than consumed during the stabilization process. They also protect polymers from thermal degradation and can be used as thermal stabilizer.

There can be made combinations of HALS of the group consisting of; HALS UV Absorber, CHIMASSORB® 119 FL, CHIMASSORB® 81, CHIMASSORB® 2020 TINUVIN® 213, CHIMASSORB® 944, TINUVIN® 234, TINUVIN® 111,TINUVIN® 326, TINUVIN® 123, TINUVIN® 328, TINUVIN® 494 AR, TINUVIN® 329, TINUVIN® 622, TINUVIN® 360, TINUVIN® 765, TINUVIN® 571, TINUVIN® 770, TINUVIN® 1577, TINUVIN® 783, TINUVIN® P, TINUVIN® 791, TINUVIN® P, TINUVIN® B 75,TINUVIN® NOR™ 371, TINUVIN® XT 833 and TINUVIN® XT 850

A preferred HALS absorber herein is Tinuvin 494.

Tinuvin 494 and above listed HALS absorbers also comprises as it is a composition of chemicals; also lipophilic groups such as but not limited to; lauric acid, myristic acid, palmitic acid and stearic acid. These are known in the prior art. The prior art is using Tinuvin 494 to prevent yellowing of polyethylene when exposed to UV light or insecticides such as deltamethrin (in greenhouses for example where such insecticides are used and evaporate and contact the plastic tunnels made of polyethylene) and in the herein described invention and art of compositing release compositions help to control the release of insecticides to the polyethylene yarn surface. Such characteristics of HALS can also be obtained by using Zinc stearate also working as a retarder.

For thermal stabilization of products and especially in combination with insecticides are used anti-oxidants such as phosphits and phenols (these are named Irganox by the Ciba Geigy company.

During an additive life cycle, the additive, as well as its components, is exposed to numerous factors that can contribute to the degradation of the additive. These factors can lead to manu-

facturing problems and reduced shelf life. Product consistency and reliability are necessary considerations for the manufacture, storage stability and service life of additives, sealants and their raw materials. Additives and its raw materials can undergo degradation, initiated by exposure to high temperatures, prolonged exposure to oxygen, mechanical shear or exposure to light. Any one of these factors can lead to an undesirable change in physical properties of the unstabilized additive. These changes can result in manufacturing problems, poor product appearance or a reduction of additive strength.

Ciba® IRGANOX® antioxidants interrupt the degradation process and help to prevent or retard all the undesirable changes.

Thermal stabilizers can be elected form the group consisting of IRGANOX® B 215 IRGANOX® 245 IRGAFOS® 38, IRGANOX® B 225, IRGANOX®, 565 IRGAFOS® 126, IRGANOX® B, 1171 IRGANOX® 1010, IRGAFOS® 168, IRGANOX® PS 800 IRGANOX® 1035 IRGANOX® PS 800, IRGANOX® 1076, IRGANOX® PS 802, IRGANOX® 1098, IRGANOX® 1135, IRGANOX® 1520 Land IRGANOX® 1726.
Most preferred are Irganox 225 and Irganox 110.

In a preferred combination of stabilizers, herein the inventor uses a package of stabilizers including steric hindered phenol with a combination of HALS molecules and phosphits, phosphonits and/or thio-co-stabilisers. The active ingredient may also destabilize the HALS molecule and thereby be destroyed itself. Specially stabilized HALS additives that do not interact with the active ingredients e.g. insecticide can be identified from additive producers.

Preferred amount is between 0,001 and 5 %; optimum effect is obtained by adapting the package to the process temperature and the concentration of active ingredients and UV filter, with most preferred concentration is 0.6% Irganox 225. It is also known that the use of Irganox 225 helps to reduce the losses of deltamethrin during the extrusion process.

Component D

Component D are UV-filters. UV filters include hydroxy-benzophenons, benzophenons, benzoxyazinones, oxalanids, benzo-triazoles as 2-hydroyxyphenyl-benzotriazol, phenyltriazines as 2-hydroyxyphenyl-triazine, and pigments like carbon black and zinc or titanium oxides. It is of course important that the absorbing spectrum of the UV filter covers the absorbing spectrum of the active ingredient(s) and/or the synthetic polymer. Where several active ingredients are used, several UV filters are applied. The higher the UV filter concentration, the better the protection. Preferred is a combination of UV filter and anti-oxidant (e.g. a HALS) for longer protection by synergistic effect. Most preferred is to use combinations of UV filters and stabilisers that concentrate near and on the surface where the active ingredient is most exposed to

UV degradation. This can be obtained with hydroxy-benzophenons that migrate in the synthetic polymer and bloom at the surface combined with small HALS molecules that add to the surface protecting effect. The package of stabilizers must then also have bigger molecules of HALS (oligomer HALS) to provide continuous protection of the synthetic itself. Also preferred are photo-reactive HALS molecules that are activated by UV light and thus provide high protection just below the surface of the material, where they are fixed after migration from deeper layers of the material.

Preferred concentrations of UV filters and stabilizers are 0,001 to 10 %, higher in intermediary products as master batches combined with pyrethroids.

Component E

Components E are Anti-migration agents. Migration barrier molecules or pigments are used to reduce the rate of blooming of the active ingredients and migrating UV filer or stabilizer. Metallic salts and crystalline accelerating additives can be used for such effect.

Component F

Components F are migrating accelerating agent and agents that improve insecticide or acaricide active ingredient to the target.

Component G

Component G are additives that increase the solubility of the insecticide in the polymer thus to reduce blooming and obtain that the surface concentration of the insecticide comes into an equilibrium with the insecticide inside the yarn. Without such additives, the surface concentration cannot be controlled over time but will continue to increase. Oils, waxes and additives of such character will work as solubility enhancers provided they are soluble in the polymer and the insecticide is soluble in the additive.

Polymer composition

A special solution may be that one yarn is a polyethylene and the other a polypropylene. Generally, the two polymers are from the same type, but with different chain lengths and branching to obtain different density and crystalline structure and thus different glass points. It is the difference between the actual temperature and the glass point that determines the driving force of the migration to the surface. The polymer composition influences the migration rate of an additive in two ways: first by influencing the solubility of the additive and second by influencing the glass point of the total compound.

Yarns are composed of filaments. The filaments can as said above be coated or incorporated with active ingredients.

A suitable example of a filament is a polymer such as a polymer chosen from the group consisting of polyester, polyethylene, polypropylene, polyacrylic, polyphtalates, polyurethane and co-polymers made of these.

In a preferred embodiment the textile product is a textile product, wherein the two different yarn or filament types both comprise at least one polymer selected from the group consisting of: polyester, polyethylene, polypropylene, polyacrylic and polyurethane; and wherein the polymers are different in the two different yarn or filament types.
More preferably, the polymers of the first yarn or filament type are comprising approximately equal amounts of high density polyethylene (HDPE) and linear low-density polyethylene (LLDPE); and the polymers of the second yarn or filament type are comprising at least 6 times more of high density polyethylene (HDPE) than linear low-density polyethylene (LLDPE).
In example 5 is shown an example of such a preferred textile product.

As explained herein, one may use different ratios of HDPE to LLDPE in the first yarn or filament type and in the second yarn or filament type.

A preferred embodiment is 1:1 (HDPE:LLDPE) in case one prefers using as described herein one insecticide in the first yarn or filament and another but not the same insecticide in a second filament or yarn. Such 1:1 HDPE/LLDPE textile products are preferably knitted.

In case woven, there are many choices possible and also all ratios preferably from 2:1 to 1:8, such as 1:1 to 1:6 LLDPE/HDPE may be used independently in the first yarn or filament type and in the second yarn or filament type. Many different ratios may be used particularly in case where filaments are twisted together into yarns and textile products are made of such yarns.

Active ingredients

Ideally, one insecticide or repellent has some repellent or contact-irritancy effect or a fast knock down effect, thus to provide personal protection (in practice this is generally pyrethroids, carbamates and repellents). The other active ingredient can be insecticide, an insect repellent or a chemosterilant – a point being that if the mosquito overcomes the first barrier, at least it will not spread the disease or (sterilant) not generate a new generation.

Suitable examples of an insect repellent is a insect repellent selected from the group consisting of DEET (N, N-diethyl-m-toluamide), essential oil of the lemon eucalyptus and its active ingredient p-menthane-3,8-diol (PMD), Icaridin, citronella oil, soybean oil and neem oil.

A chemosterilant may be a sterilant that prevent the mosquito to contribute to the next generation and thus also has a mass effect, but no transmission effect.

A more preferred embodiment is a combination of a fast acting insecticide or repellent to give a personal protection and a synergist or alternative insecticide that result in a killing of insects in contact with the net and thus stop further transmission and provides a “mass effect” by reducing the vector population.

As examples of the first, one insecticide is a pyrethroid like deltamethrin and the other is pirimiphos methyl, where the insecticide resistance mechanism is Kdr.

In another example, the first insecticide is a pyrethroid and the second is piperonyl butoxide where the insecticide resistance mechanism is an oxidase mechanism.

In a third example, the first insecticide is a pyrethroid and the second is fipronil, where there is resistance to pyrethroids and to organophosphates, e.g. based on esterase, oxidase and changed acetylcholine esterase as resistance mechanisms. As apparent from these examples, a best combination is based on knowledge of the resistance pattern of the malaria vector and nuisance mosquitoes in the target area.

Piperonyl butoxide (PBO) is an example of a pesticide synergist. A synergist is an active ingredient that is added to an insecticide product, in addition to the active and inert ingredients, to increase the potency of the active ingredient. In this context is it used as a separate active ingredient in filaments or yarns and increases the potency of the insecticide as it weakens detoxifying mechanisms of insects of course especially relevant to resistant insect populations which have many of such detoxification mechanisms against multiple insecticides.
For instance, when added to insecticide mixtures, typically pyrethrin, pyrethroid, and carbamate insecticides, their potency is increased considerably.

The insecticide works by contact, not only by oral ingestion. It may work as a fast paralyzing insecticide or as a slow acting killing insecticide or as sterilizing agent. The insecticide may possess repellent or deterrent activity and this may be the main principle. It must have low mammalian toxicity. Suitable insecticides are known by persons skilled in the art. They may be the insecticides listed below, or belong to the same or other groups. Especially, some insecticides and repellents are used as synergistic or at synergistic dosages and can be used in blends.

Preferred insecticides may belong to the group pyrethroid compounds such as ethofenprox: 2-(4-ethoxyphenyl)-2-methylpropyl-3-phenoxybenzyl ether; Fenvalerate: (RS)-alpha-cyano-3-phenoxybenzyl (RS)-2-(4-chlorophenyl)-3 methylbutyrate; Esfenvalerate:(S)-alpha-cyano-3-phenoxybenzyl (S)-2-(4-chlorophenyl)-3-methylbutyrate; Fenpropathrin: (RS)-alpha-cyano-3-phenoxybenzyl 2,2,3,3-tetramethylcyclopropanecarboxylate; Cypermethrin: (RS)-alpha-cyano-3-phenoxybenzyl (1RS)-cis, trans-3-(2,2-dichlorovinyl)-2,2- dimethylcyclopropanecarboxylate; Permethrin: 3-phenoxybenzyl (1RS)-cis,trans-3-(2,2-dichlorovinyl)-2,2- dimethylcyclopropane-carboxylate; Cyhalothrin: (RS)-alpha-cyano-3-phenoxybenzyl (Z)-(1RS)-cis-3- (2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopro panecarboxylate; Deltamethrin: (S)-alpha-cyano-3-phenoxybenzyl (1R)-cis-3-(2,2-dibromovinyl) -2,2-dimethylcyclopropanecarboxylate; Cyclo-prothrin: (RS)-alpha-cyano-3-phenoxybenzyl (RS)-2,2-dichloro -1-(4-ethoxyphenyl)-cyclopropanecarboxylate; Fluvalinate (alpha-cyano-3-phenoxybenzyl N-(2-chloro-alpha,alpha,alpha-trifluoro-p-tolyl) -D-valinate); Bifenthrin: (2-methylbiphenyl-3-ylmethyl)0(Z)-(1RS)-cis-3-(2-chloro-3,3,3-trifluoro-1-propenyl) -2,2-dimethylcyclopropanecarboxylate; 2-methyl-2-(4-bromodifluoromethoxyphenyl) propyl (3-phenoxybenzyl) ether; Tralomethrin: (S)-alpha-cyano-3-phenoxybenzyl (1R-cis)3((1'RS)(1',2',2',2'-tetrabromoethyl)) -2,2-dimethylcyclopropanecarboxylate; Silafluofen: 4-ethoxyphenyl (3-(4-fluoro-3-phenoxyphenyl)propyl}dimethylsilane; D-fenothrin: 3-phenoxybenzyl (1R)-cis, trans)-chrysanthemate; Cyphenothrin: (RS)-alpha-cyano-3-phenoxybenzyl (1R-cis, trans)-chrysanthemate, D-resmethrin: 5-benzyl-3-furylmethyl (1R-cis, trans)-chrysanthemate; Acri-nathrin: (S)-alpha-cyano-3-phenoxybenzyl (1R-cis(Z))-(2,2-dimethyl-3- (oxo-3-(1,1,1,3,3,3-hexafluoropropyloxy)propenyl (cyclopropanecarboxylate; Cyfluthrin: (RS)-alpha-cyano-4-fluoro-3-phenoxybenzyl 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate; Tefluthrin: 2,3,5,6-tetrafluoro-4-methylbenzyl (1RS-cis (Z))-3-(2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarbo xylate; Transfluthrin: 2,3,5,6-tetrafluorobenzyl (1R-trans)-3-(2,2-dichlorovinyl) -2,2-dimethylcyclopropane-carboxylate; Tetramethrin: 3,4,5,6-tetrahydrophthalimido-methyl (1RS)-cis, trans-chrysanthemate; Allethrin: (RS)-3-allyl-2-methyl-4-oxocyclopent-2-enyl (1RS)-cis, trans-chrysanthemate; Prallethrin: (S)-2-methyl-4-oxo-3-(2-propynyl)cyclopent-2-enyl (1R)-cis, trans-chrysanthemate; Empenthrin: (RS)-1-ethynyl-2-methyl-2-pentenyl (1R)-cis,trans-chrysanthemate; Imiprothrin: 2,5-dioxo-3-(prop-2-ynyl)imidazolidin-1-ylmethyl (1R)-cis; trans-2,2-dimethyl-3-(2-methyl-1-propenyl)-cyclopropanecarboxylate; D-flamethrin: 5-(2-propynyl)-furfuryl (1R)-cis, trans-chrysanthemate, or 5-(2-propynyl)furfuryl 2,2,3,3-tetramethylcyclopropane-carboxylate.

Therefore, in a preferred embodiment, one filament can comprise a pyrethroid (such as e.g. deltamethrin, permethrin or bifenthrin), and the other filament a piperonyl butoxide. These can be incorporated into filaments and thereafter spun into yarns.

Another embodiment is a first filament or yarn comprising a pyrethroid insecticide and the second filament or yarn comprising a repellent. The choice of active ingredients (insecticide or reppellent) and type of textile nets (net, ground cover, film) is dependent on the country (type of climate), insects (climate zones), which targets (malaria insects or food damaging insects) and which type of resistance these insects already have.

Methoprene is a juvenile hormone (JH) analog, which can be used as an insecticide that acts as a growth regulator. Methoprene does not kill adult insects. Instead, it acts as a growth regulator, mimicking natural juvenile hormone of insects. Juvenile hormone must be absent for a pupa to molt to an adult, so methoprene treated larvae will be unable to successfully change from a pupa to the adult insect. This breaks the biological life cycle of the insect preventing recurring infestation. Methoprene is considered a biochemical pesticide because rather than controlling target pests through direct toxicity, methoprene interferes with an insect's life cycle and prevents it from reaching maturity or reproducing.

In general, such biochemical pesticides can be used in this context. One filament may be incorporated with a synthetic analog such as a chemosterilant or a juvenile hormone (e.g. Methoprene) and the other filament may comprise an insecticide. This strategy will reduce or influence the development and further spreading of multi-resistant insects in following generations.

Insects are capable of developing resistance, and mosquitoes and other biting insects have already been observed to develop resistance to pyrethroids. In such cases, it may be advantageous to replace the pyrethroid with another insecticide with a low mammalian toxicity or to impregnate a part of the material net with a pyrethroid and a part of it with another insecticide. Such a combination may also be used in general as a strategy to delay resistance development. Care should be taken to combine insecticides that have little or no chance to develop cross resistance, e.g. where the development of resistance to one of them also confer resistance to the other even the two insecticides are of different type. Such alternative or supplemental insecticides may be compounds such as organophosphorous compounds organophosphorous compounds such as: Fenitrothion: O,O-dimethyl 0-(4-nitro-m-tolyl) phosphorothioate; Diazinon: 0,0-diethyl-0-(2-isopropyl-6-methyl-4-pyrimidinyl) phosphorothioate; Pyridaphenthion: 0-(1,6-dihydro-6-oxo-1-phenylpyrazidin-3-yl) 0,0-diethyl phosphorothioate,; Pirimiphos-Etyl: 0,0-diethyl 0-(2-(diethylamino) 6-methyl-pyrimidinyl) phosphorothioate; Pirimiphos-Methyl: 0-[2-(diethylamino)-6-methyl-4pyrimidinyl] 0,0-dimethyl phosphorothioate; Etrimphos: 0-6-ethoxy-2-ethyl-pyrimidin-4-yl-0,0-dimethyl-phosphorothioate, Fenthion: 0,0-dimethyl-0-[-3-methyl-4-(methylthio) phenyl phosphorothioate, Phoxim: 2-(diethoxyphosphinothoyloxyimino)-2-phenylacetonitrile; Chlorpyrifos: 0,0-diethyl-0-(3,5,6-trichloro-2-pyrinyl) phosphorothioate; Chlorpyriphos-methyl: 0,0-dimethyl 0-(3,5,6-trichloro-2-pyridinyl) phosphorothioate; Cyanophos: 0,0-dimethyl 0-(4cyanophenyl) phosphorothioate; Pyraclofos: (R,S)[4-chlorophenyl)-pyrazol-4-yl] -0-ethyl-S-n-propyl phosphorothioate; Acephate: 0,S-dimethyl acetylphospho-

roamidothioate; Azamethiphos: S-(6-chloro-2,3-dihydro-oxo-1,3-oxazolo [4,5-b] pyridin-3-ylmethyl phosphorothioate; Malathion: 0,0-dimethyl phosphorodithioate ester of diethyl mercaptosuccinate; Temephos: (0,0'(thiodi-4-1-phenylene) 0,0,0,0-tetramethyl phosphorodithioate, Dimethoate: ((0,0-dimethyl S-(n-methylcarbamoylmethyl) phosphorodithioate, Formothion: S[2-formylmethylamino]-2-oxoethyl]-O,O-dimethyl phosphorodithioate; Phenthoate: 0,0-dimethyl S-(alpha-ethoxycarbonylbenzyl)-phosphorodithioate.

Furthermore, carbamate compounds may be applied including compounds such as: Alanycarb: S-methyl-N[[N-methyl-N-[N-benzyl-N(2-ethoxy-carbonylethyl) aminothio]carbamoyl]thioacetimidate; Bendiocarb: 2,2-dimethyl-1,3-benzodioxol-4yl- methylcarbamate); Carbaryl (1-naphthyl N-methylcarbamate); Isoprocarb: 2-(1-methylethyl) phenyl methylcarbamate; Carbosulfan: 2,3 dihydro-2,2-dimethyl-7-benzofuranyl [(dibutylamino)thio] methylcarbamate; Fenoxycarb: Ethyl[2-(4-phenoxyphenoxy)ethyl] carbamate; Indoxacarb: Methyl-7-chloro-2,3,4a,5-tetrahydro-2-[methoxycarbonyl (-4-trifluoromethoxyphenyl)]; Propoxur: 2-isopropyloxyphenol methylcarbamate; Pirimicarb: 2-dimethylamino-5,6-dimethyl-4-pyrimidinyl- dimethylcarbamate; Thidiocarb: Dimethyl N,N'(thiobis((methylimino)carbonoyloxy) bisethanimidiothioate); Methomyl: S-methyl N-((methylcarbamoyl)oxy)thioacetamidate; Ethiofencarb: 2-((ethylthio)methyl)phenyl methylcarbamate; Fenothiocarb: S-(4-phenoxybutyl)-N,N-dimethyl thiocarbamate; Cartap: S,S'-(2-5dimethylamino)trimethylene)bis (thiocarbamate)hydrochloride; Fenobucarb: 2-sec-butylphenylmethyl carbamate; XMC: 3,5-dimethylphenyl-methyl carbamate; Xylylcarb: 3,4-dimethylphenylmethylcarbamate.

Newer insecticides with lower mammalian toxicity at use dosage are interesting alternatives, especially because vector insects rarely have developed resistance to these. Such new groups of insecticides are pyramidialmines (Pyrimidifen), Pyrazoles (Fipronil and Fenpyroxiamte), Pyrrols (clorfenapyr), dicloproamid. Chlorphenapyr is especially interesting since it has been used experimentally (Rowland et al, 2005) and shown interesting, though slow effect.

Where nets and other impregnated materials are used in mass campaigns, the alternative or supplemental insecticide may also be an insecticide with a sterilizing effect thus to sterilize the mosquitoes and avoid the next generation of mosquitoes. Such insecticides can be of the benzoyl urea group such as 1-(alfa-4-(chloro-alpha-cyclopropylbenzylidenamino-oxy)-p-tolyl)-3-(2,6-diflourobenzoyl)urea, Diflubenzuron: N-(((3,5-dichloro-4-(1,1,2,2-tetraflouroethoxy)phenylamino) carbonyl)2,6 diflouro benzamid, Triflumuron: 2-Chloro-N-(((4-(triflouromethoxy) phenyl)-amino-)carbonyl) benzamide, or a triazin such as N-cyclopropyl-1,3,5 -triazine-2,4,6-triamin or other insecticides with a sterilizing effect on adult mosquitoes.

Another way to overcome resistance problems is the traditional use of synergists. Piperonyl

butoxid and sesamex are traditionally used to combine with pyrethroids to overcome enzymatic based resistance mechanisms. Further DEET, usually used as a repellent, has shown to have synergistic abilities to organophosphorous and Carbamates, but is difficult to integrate for a prolonged effect due to its high vapor pressure (Vincent et al, 2004). Other biocides may show synergistic effect due to their interaction with detoxifying resistance mechanisms. Integrating of such biocides that maybe are registered as insecticides may be included provided they are not innate unstable or with high vapor pressure.

The repellent may work in a mixture with the insecticide or acaricide or by its own abilities. Repellent are selected from DEET: N,N-Diethyl-meta-toluamid; DEPA (N,N-diethylphenylacetamid; 1-(3-cyclohexan-1-yl-carbonyl)-2-methylpiperine; (2-hydroxymethylcyclohexyl); acetic acid lactone; 2-ethyl-1,3-hexandiol; indalone; MDNA: Methyl-neodecanamide; and pyrethroids not used as insecticides such as Esbiothrin: {(+/-)-3-ally62-methyl-4-oxocyclopent-2-(+)-trans-chrysanthemate.

Pyrethroids and some repellants have chiral centers giving rise to two to several racemates or isomers. The list above also includes existing and chiral derived isomers, racemates and pure enatiomers or diasteomers produced to give enhanced effect or to reduce the insecticidal or mammalian toxicity while increasing a specific activity as durability, repellent or deterrent effect or narrowing the activity to a special groups of target insects or acarinae.

Herbicides, especially algacides, and bacteriocides or bacteriostatics may be integrated to prevent growth of algae and bacteria on the final product. A person skilled in the art can select among these from criteria of thermal stability, solubility in oil, low mammalian toxicity and low vapor pressure. Negative, chemical interactions between active ingredients should be avoided.

The active ingredients in from of insecticide, acaricide, biocide, repellant, herbicide, bactericide or bacteriostatic mentioned in the present invention may be included in technical grade in a master batch in powder, granular or fluid form or added to the basic synthetic material just after it's polymerization. These intermediate forms are also included in the present invention. The active ingredients may also be added undiluted or diluted with inert material directly to the final process step when forming the yarn fibre or film. When more than one insecticide, acaricide, biocide, repellant, herbicide, bactericide or bacteriostatic are added, they may be added during various step of the production process. Some active ingredients are very temperature stable and can be added just after polymerization of the synthetic, whereas other active ingredients can only by added later in the production process to avoid evaporation or destruction. Such addition may be in the latest stage of the extrusion or post extrusion in the form of a coating. Modern extruders can be combined so that the same spinerette is fed by two extrud-

ers each carrying a different insecticide and produce different filaments yarns thereby carry different insecticides before the yarn is formed e.g. by twisting. Several ingredients may be added mixed or in separate master batches before mixing into the final mass for production, often as extrusion. Additives to protect the active ingredients against destruction in the intermediary or final production process can of course with advantage already be mixed into these intermediary forms as a master batch.

A typical amount of active ingredients is between 0.001 and 5% (dry weight) of the (dry) weight of the fabric or netting dependent on the insecticidal efficacy of the insecticide. A preferred amount is between 0.05 and 1 % of the fabric or netting dependent on the insecticide.

For a pyrethroid like deltamethrin or alpha-cypermethrin, the preferred amounts are between 0.05 and 0.3 % of the weight of fabric or netting. For a pyrethroid like permethrin or etofenprox or an insecticide like chlorfenapyr, the preferred amounts are between 0.1 and 6 %.

When the synthetic filament fibre or yarn are mixed with non impregnated yarns or filaments of synthetic or natural origin, the concentrations may be higher to obtain a proper level of insecticide or biocide at contact points for the target insect or acarinae. When the active ingredients are mixed into intermediary phases like a masterbatch, the concentration is typically 10-100 times higher than in the final product.

Insecticide resistance

As the literature indicates, insecticidal treated bednets with only one insecticide are getting less effective due to the increasing development of resistant insect populations. Intradomicial house spraying and bednets mostly use pyrethroids or DDT, but DDT is also counteracted by the kdr resistance mechanism. Therefore, when the Roll Back Malaria campaign mostly use these tools for vector control, the whole campaign risk to collapse as did the earlier campaign in the 1960's, where mostly DDT was used and resulted in high levels of resistance in India, where the campaign in the start was very successful.

As insecticidal bednets are more and more used for the prevention of malaria (more than 100 million nets per year are distributed to prevent malaria), the insects are increasingly exposed to the same active ingredients such as deltamethrin and permethrin. As a result, malaria vector control is getting less effective. Some publications such as Guillet et al and C. Pennetier indicate that the concept of using two insecticides has some perspectives for the control of malaria vectors. However, as the authors also indicate, the step to real life implementation such a new textile product needs to be invented with such functions.

Several insecticide resistance mechanisms are described for malaria vectors. A modification in the receptor for pyrethroids and DDT, the voltage gated sodium channel, can undergo single point genetic modifications that reduce the insecticide susceptibility and reduce the knock down effect of these insecticides, hence called knock down resistance abbreviated kdr. Kdr resistance is now wide spread in West and Central Africa (Reimer et al, 2008). These and several other insecticides are also susceptible to oxidases that enzymatically destroy the absorbed insecticide and are found in West Africa. Gluthathion transferase is another enzymatic resistance mechanism that provides resistance to DDT in Zanzibar and Mexico (Laiaied et al;, 1995, Penilla et al, 1998). Local resistance patterns to insecticides reveal exposure to adults for mosquito control, but also for larval exposures to run off from agricultural insecticide applications (Dabate et al, 2002). Resistance management is thus complex and must take actual data into consideration and not hypothesize a general solution. This impact the choice of insecticide combinations in textiles used for vector control.

The same resistance problems occur in agriculture and use of pesticides for crop protection. Such textile products as discussed herein are also widely used in agriculture. Particular applications of textile products are nets used for the protection of crops grown outdoor or indoor. Indoor grown crops are typically tomatoes, peppers or cucumbers. Such indoor crops are basically grown in greenhouses where textile products such as nets (with specific meshes) or tunnels (films of e.g. polyethylene and/or polypropylene) or partially net and/or films are protecting the crops. Typically, the entire greenhouse is build of plastic/polymer materials. These are widely used in warmer areas e.g. Spain (Almeria or Murcia) where the major winter vegetables are grown for export to northern countries especially in winter times.

As these areas do not have a cold winter, there is non- stop generations of insects may be 8 to 12 cycles yearly which also increases the risk of resistance. Typical crop damaging insects are white flies and aphids, e.g. species such as Bemisia tabaci or Bemisia argentifolii. Nets according to the present invention can protect crops particularly in the following way: Especially white flies' damage is both sucking damage on the crop but more seriously the transmission of virus. In case, a textile product comprises, as present invention describes, one yarn with an insecticide for example a pyrethroid and the other yarn with a repellent, such transmission may be prevented effectively.

The reason is that white flies already have a high level of resistance as known. It is very difficult to find more effective insecticides against white flies, thus even if they, at the point of contact are irritated or partially "burned" due to contact with the insecticide, they still can enter the crop area and before they are killed, still transmit the virus into the crop.

In reality, the most important thing may even not be to kill the insect but to prevent entering, in

fact these insects are not killed instantly, and therefore may transfer virus to the crop upon entering. Note that none insecticide treated nets are used also to prevent entry of insects but there the mesh size is relevant. If the mesh size is chosen to small to make a physical barrier then the temperature inside the greenhouses increases unacceptably e.g. over 40ºC which is then damaging the crop. The combination of one yarn or filament type having an insecticide and the other yarn or filament type a repellent is therefore of specific interest for agricultural textile products.

Therefore, a preferred embodiment is a textile product where one yarn or filament type comprises an insecticide such as pyrethroid and the other yarn or filament type comprises a repellent. Such yarns or filament types may be knitted or woven together and may be made into textile products with different mesh size openings.

The same applies for other textile products useful in agriculture such as ground cover nets or also named push up nets. These are nets used to cover the early seedlings, well known by the skilled person. Present invention can be applied to make ground covers comprising one yarn with one insecticide and the other a repellent and have similar release rates.

Other type of agricultural used textiles products are; shade nets, textile products are greenhouse sides or simply the entire greenhouse as a net, ventilations nets films or so-called tunnels in glasshouses covering crops, ground cover, insect screens for houses as windows or doors , mosquito nets as such for wearing and tents made of nets.

<u>Release rate of different active ingredients - not significantly different</u>

In example 3 is provided detailed instructions on how to measure if the release rate of the two different active ingredients are essential the same – as required in point (b) of the first aspect.

Essentially the method of example 3 relates to measurement of slope of decay for the two different active ingredients. If the Confidence is at least 90% - it is believed that the release rate for the two different active ingredients is sufficient similar to solve the problem as described herein – i.e. reducing the development of insecticide resistance.

All individual measurement steps of example 3 may be considered as standard routine steps for the skilled person. Accordingly, by following example 3 it is routine work for the skilled person to determine if a textile product of interest fulfills the criteria of point (b) of the first aspect.

In preferred embodiment, the Confidence of point (b) is at least 92%, more preferably the Confidence of point (b) is at least 95%.

A method to manufacture a textile product as described herein

As said above, the second aspect of the invention relates to a method to manufacture a textile product of the first aspect comprising the following steps:

(Ia): making a first yarn type that release at least one active ingredient selected from the group consisting of an insecticide and a second yarn type that release at least one active ingredient, but not the same as the first yarn, selected from the group consisting of an insecticide, an insect repellent and a chemosterilant;

or

(Ib): making a yarn comprising at least two different filament types spun into the yarn characterized by that:

(i): the first filament type releases at least one active ingredient selected from the group consisting of an insecticide and the second filament type releases at least one active ingredient, but not the same as the first filament type, selected from the group consisting of an insecticide, an insect repellent and a chemosterilant;

and

(IIa): weaving or knitting parts of the textile product comprising the first type of yarn with one active ingredient and other parts with the second type of yarn comprising another different active ingredient (in case of step Ia) ;

or

(IIb) weaving or knitting the textile product by mixing the yarn types (in case of step Ia) or the yarn type (in case of step IIb) randomly in all relevant parts of the textile product;

and

(III) cut the textile product and shape it into a bednet, tarpaulin or any given shape fitting the end use.

As understood to the skilled person, all the steps as such of the method are routine steps known to the skilled person.

In a suitable example is used option (IIb) in step (II).
When option (IIb) in step (II) is used the textile product may e.g. comprise at least 50% of such randomly woven or knitted part.

In another suitable example is used option (IIa) in step (II).

Detailed embodiments

Embodiment 1: a textile product to kill insects,

(1a): wherein the textile comprises at least two different yarn types characterized by that:

(i): the first yarn type releases at least one active ingredient selected from the group consisting of an insecticide and the second yarn type releases at least one active ingredient, but not the same as the first yarn, selected from the group consisting of an insecticide, an insect repellent, pesticide synergist and a chemosterilant;

or

(1b): wherein the textile comprises a yarn comprising at least two different filament types spun into the yarn characterized by that:

(i): the first filament type releases at least one active ingredient selected from the group consisting of an insecticide and the second filament type releases at least one active ingredient, but not the same as the first filament type, selected from the group consisting of an insecticide, an insect repellent, pesticide synergist and a chemosterilant;

and wherein

(a): the two different active ingredients are both present on the surface of the yarn after 20 defined laboratory washes; and

(b): the release rate of the two different active ingredients are essential the same for both, as measured by determining the slope of the decay as described in example 3 and where the slope of decay for the two different active ingredients may not be significantly different, defined as the confidence is at least 90%.

Embodiment 2 is the textile product of embodiment 1, wherein the product is a product selected from the group consisting of net, mosquito bednet, curtain, cushion, wall covering textile, tarpaulin, cloths and window/door screen.

Embodiment 3 is the textile product of embodiment 2, wherein the product is a mosquito bednet.

Embodiment 4 is the textile product of any of embodiment 1, 2 and 3 , wherein the two different yarn or filament types both comprise at least one polymer selected from the group consisting of: polyester, polyethylene, polypropylene, polyacrylic and polyurethane; and
wherein the polymers are different in the two different yarn or filament types.

Embodiment 5 is the textile product of embodiment 4, wherein
the polymers of the first yarn or filament type are comprising approximately equal amounts of high density polyethylene (HDPE) and linear low-density polyethylene (LLDPE); and
the polymers of the first yarn or filament type are comprising at least 6 times more of high density polyethylene (HDPE) than linear low-density polyethylene (LLDPE).

Embodiment 6 is the textile product of any of embodiments 1,2,3,4, and 5, wherein the insecticide is at least one insecticide selected from the group consisting of pyrethroids, organophosphates and carbamates.

Embodiment 7 is the textile product of embodiment 6, wherein the second yarn or filament type releases at least one pesticide synergist, such as e.g. piperonyl butoxide.

Embodiment 8 is the textile product of embodiment 6, the first yarn or filament type releases at least one pyrethroid and the second yarn or filament type releases at least one carbamate.

Embodiment 9 is the textile product of embodiments 6 to 8, wherein the pyrethroid is deltamethrin or permethrin.

Embodiment 10 is the textile product of any of embodiments 1 to 9, wherein the Confidence of point (b) of claim 1 is at least 95%.

Embodiment 11 is a method to manufacture a textile product of embodiment 1 comprising the following steps:

(Ia): making a first yarn type that release at least one active ingredient selected from the group consisting of an insecticide and a second yarn type that release at least one active ingredient, but not the same as the first yarn, selected from the group consisting of an insecticide, an insect repellent and a chemosterilant;

or

(Ib): making a yarn comprising at least two different filament types spun into the yarn characterized by that:

(i): the first filament type releases at least one active ingredient selected from the group consisting of an insecticide and the second filament type releases at least one active ingredient, but not the same as the first filament type, selected from the group consisting of an insecticide, an insect repellent and a chemosterilant;

and

(IIa): weaving or knitting parts of the textile product comprising the first type of yarn with one active ingredient and other parts with the second type of yarn comprising another different active ingredient (in case of step Ia) ;

or

(IIb) weaving or knitting the textile product by mixing the yarn types (in case of step Ia) or the yarn type (in case of step IIb) randomly in all relevant parts of the textile product;

and

(III) cut the textile product and shape it into a bednet, tarpaulin or any given shape fitting the end use.

Embodiment 12 is the method of embodiment 11, wherein there is used option (IIb) in step (II).

Embodiment 13 is the method of embodiment 11, wherein the textile product comprises at least 50% of such randomly woven or knitted part.

Embodiment 14 is a textile product to kill insects of any of embodiments 1 to 10, wherein the textile product is obtainable by a method of any of embodiments 11 or 13.

Embodiment 15 is the textile product to kill insects of embodiment 14, wherein the textile product is obtainable by a method of embodiment 12 or 13.

EXAMPLES

Example 1: *Method to measure killing mosquito's in vivo (knockdown) with a sufficient insecticide dosage: (according to WHO, World Health Organization).*

The term "sufficient dosage" herein is understood as: 50, 3-4 days old female mosquitoes are exposed to textile (net) under standard WHO cones, 5 in each cone, for 3 min. The net must still be able to kill at least 80 % of mosquitoes of a susceptible (no insecticide resistance) strain of mosquitoes after 24 hours or to paralyze (called knocked down) at least 95 % within 60 min. Mosquitoes are hold in cups with sugar water available for the 24 hr, at 25±2°C and 75±10 % RH.

Alternatively, 5-8 days old adult female mosquitoes are released in a tunnel (square section 25x25 cm) made of glass, 60 cm length. At each end of the tunnel, a 25 square cm cages is fitted (extension) and covered with polyester netting. At one third of the length, a disposable cardboard frame is placed with the netting sample. The surface of the netting available to mosquitoes is 400 cm^2 (20x20 cm), with none holes each 1 cm diameter: one hole is located at the centre of the square; the other eight are equidistant and located at 5 cm from the border. In the shorter section of the tunnel, bait (guinea pig for Anopheles gambiae) is placed, unable to move. In the cage at the end of the longer section of the tunnel, 100 females are introduced at 18:00. Females are free to fly in the tunnel, but have to make contact with the net and locate holes before passing trough to reach the bait. The following morning 9:00, mosquitoes are removed and counted from each section and immediate mortality and blood feeding status is recorded. Delayed mortality is recorded on live mosquitoes transferred to cups with sugar water and after 24 hr. Mortality must be at least 80 % and blood feeding inhibition at least 90 % for a textile (net) still sufficient active. (Guidelines for laboratory and field testing of long lasting insecticidal mosquito nets, WHO/CDS/WHOPES/GCDPP/2005.11).

Example 2: *Measurement of release of insecticide on the surface of the yarn*

DETERMINATION OF DELTAMETHRIN IN POLYETHYLENE SAMPLE

The amount of insecticide (deltamethrin) is determined by the following known method to the skilled person. The methods are standard methods, well documented, validated and described in CIPAC methods and handbooks (www.cipac.org).

For extraction of deltamethrin referring to CIPAC report 4568/m, extension of CIPAC method 454 for determination of alpha-cypermethrin in DuraNet® [extraction by heating under reflux for 30 minutes with xylene in presence of dipropyl phthalate as internal standard].

For chromatographic determination of deltamethrin: CIPAC method 333/TC/M/3, CIPAC Handbook D, page 57 and extension of CIPAC method 333 for determination of deltamethrin in PermaNet® [method by High Performance Liquid Chromatography with UV/Visible Diode Array Detection (HPLC-DAD method) using the internal standard calibration].

Summary of the method:
Deltamethrin (and deltamethrin R-isomer) is extracted from samples herein coded as 195, 196 and 197 by heating under reflux for 30 minutes with xylene and determined by High Performance Liquid Chromatography with UV Diode Array Detection (HPLC-DAD) using the internal standard calibration. As Internal standard solution, about 100 mg of dipropyl phthalate are accurately weighed (to the nearest 0.1 mg) into a 200 ml volumetric flask. Xylene is added until complete dissolution. The flask is filled up to volume with xylene (= IS solution).

DETERMINATION OF PIPERONYL BUTOXIDE IN POLYETHYLENE SAMPLE
Refer to CIPAC #33

1. Chemicals
Solvent: Toluene HPLC grade, n-Hexane HPLC, 1.4 Dioxane HPLC
Mixed solvent solution: n-Hexane HPLC: 1.4 Dioxane HPLC = 95: 5

2. Preparation
Digestion
Weight about 1 gram (a gram) sample into the digested bottle
Add 20ml Toluene
Boil the digested bottle at 100°C, 1 hour; to be sure the sample is digested totally
Let the digested bottle cool down to room temperature.
Swirl the bottle to homogenize the digest liquid
Transfer totally the digested solution into the 50ml volumetric flask by toluene and fill up to mark with extraction solvent
Use the filter with pore size of 0.45μm filter about 5 ml into vial
Change in the solvent
Use a marked pipette to take exactly 1 ml extracted solution into vial
Evaporate the above extracted solution by Nitrogen gas
Use marked pipette to take 1 ml mixed solvent solution into the above vial, mix well

3. Making the standard solution
Standard solution of 10ml
Standard solution mg/ml

Piperonyl butoxide 0.0600

Level	Piperonyl butoxide (ml)	Concentration (ug)
Level 1	2	12
Level 2	3	18
Level 3	5	30
Level 4	6	36
Level 5	8	48

4. Condition of running HPLC equipment
Instrument: HPLC
Column: Si 15cm
Flow: 1.0 ml / min
MP: n-Hexane HPLC: 1.4 Dioxane HPLC = 95: 5
Inject volume: 5µl
Wavelength: 254nm
Run time: 8 min

5. Calculation:
Piperonyl butoxide concentration is [Piperonyl butoxide](mg/g) = reading(ug) * 50/1000/ a

Example 3: *Slope of decay*

When two insecticides (or one insecticide and a synergist or repellent) are used to reduce resistance development or to overcome resistance already developed, it is important for the effect of the textile that these remain present during the lifetime of the product and in ratios that are quite constant over this time. Therefore, the percentage loss of the two active ingredients must be approximately the same to obtain that the ratio of surface concentrations of the two remain stable. This is measured by exposing the textile to washings as described in WHO guidelines 2005 (reference 4 herein) and measure the concentration of the two (or more) active ingredient after 0, 5, 10, 15, and 20 washes. The slope of the decay curves may not be significantly different. By significant difference is meant that the data are simply tested for statistically differences using a T-test as known by the skilled person and wherein the 0 hypothesis is that the two decay curves are parallel (no differences) and if that hypothesis is rejected, the curves are not parallel and decay is therefore different, meaning that one insecticide is released before the other.
Figure 1 and 2 show this clearly graphically as a theoretical example. First, the concentration of release of insecticide is measured on the surface of the yarn as described under example 2. Then, the textile product is washed according to the method described guidelines WHO

2005, and after each wash, the surface concentration is measured. After for example 15 washes decay becomes visible when plotting amount of washing cycles (X-axis) against Y-axis (see now figure 1). The data produced as described above to produce figure1, can then be logarithmically transformed and plotted again, which represents figure 2. The lines are obtained in figure 2 can be statistically analyzed with a T-test as known by skilled persons in the art. The T-test a zero hypothesis which is the one where the lines are parallel (no differences) or if the zero hypothesis is rejected, are no parallel (different from each other). In the T-test is the Confidence set to 90% or also understood by the skilled person Type I error or Alpha risk =10%.

Example 4: *Textile product made by using same yarn (comparative example)*

Textile products for the protection of humans or animals against nuisance insects such as causing malaria (mosquitoes) are typically made of polyethylene, polypropylene and/or mixtures thereof. Both polyethylene and polypropylene can be used for the preparation of yarns.

Examples of yarns described herein by means of example are made up with polyethylene and are all monofilaments.

Release compositions which are the same for the different insecticides used in yarns

The release composition recipes are the same for the three samples discussed herein; 195, 196 and 197. The only difference is of course the insecticide, e.g. for sample 195, recipe as below using insecticide piperonyl butoxide, for sample 196, deltamethrin and piperonyl butoxide in the same yarn and for sample 197 deltamethrin and piperonyl in separate yarns than combined to a yarn and made into a textile product.

The following amount of insecticide (expressed in gram per kg master batch) was used in the samples:

Sample 195:
Release composition with piperonyl butoxide in an amount of 1.34 g piperonyl butoxide/kg.

Sample 196:
Release composition with deltamethrin in an amount of 1.9 g/kg

Sample 197
Release composition with both piperonyl butoxide and deltamethrin in amounts of 1.34 g piperonyl butoxide and 1.9 g deltamethrin/kg.

Release composition is a composition of following known to the skilled person additives and are;
Chemissorb 81: 4 g/kg
Tinuvin 494: 7 g/kg
Irganox 225: 0.64 g/kg.

The release composition as described above is than blended with polyethylene in the following ratio's of insecticide, polyethylene and additives (release components) than termed masterbatches; masterbatches are 1 kg LLDPE with insecticide, 2 kg LLDPE with additives and 25 kg HDPE. Without any other modifications of the polymer blend, it is not expected to give a constant ratio of Deltamethrin release to the surface.

LLDPE is linear low-density polyethylene (LLDPE) is a substantially linear polymer (polyethylene), with significant numbers of short branches, commonly made by copolymerization of ethylene with longer-chain olefins. Linear low-density polyethylene differs structurally from conventional low-density polyethylene because of the absence of long chain branching.

HDPE is high density polyethylene and typically has little branching, giving it stronger intermolecular forces and tensile strength than lower-density polyethylene. It is also harder and more opaque and can withstand somewhat higher temperatures (120 °C/ 248 °F for short periods, 110 °C /230 °F continuously).

All ingredients are mixed and the mix is poured into extruder and the extruder ran at 200°C as know to the skilled person when this particular application of technology (insecticide comprising yarns) is applied. For normal extrusion (without insecticides, synergists or chemosterilant) of polyolefin's 250 °C is used as known to the skilled person.

	SE1(mg/g)		SE2(mg/g)	
Sample code	Deltamethrin Yarn-1	Piperonyl butoxide Yarn-1	Deltamethrin Yarn-1	Piperonyl butoxide Yarn-1
195 replicate 1	0.000	0.0124	Not detected	0.0408
195 replicate 2	0.000	0.0190	Not detected	0.0394
195 average 1 and 2	**0.000**	**0.0157**	Not detected	**0.0401**

Table 1: Data in table 1 show rapid release of piperonyl butoxide in the absence of deltamethrin. SE means surface extraction as described in example 4. SE is measured according to method described under example 2.

Data in table 1 shows a rapid release of piperonyl butoxide. The rapid release can be seen by comparing SE1 (extraction at time 1) with SE2 (extraction at time 2). A first extraction (SE1) removes a first layer of piperonyl butoxide. The net is then stored at 30°C for a week and a second layer is formed. This layer contained 4 times the amount as compared to extraction time 1 (0.0124 SE1 with 0.0408 SE2 time 2). As can be concluded, with time, piperonyl butoxide will leave rapidly and even at increased speed. Surface insecticide is extracted with hexane (Cipac 331/LN/M/4) that will not extract from the yarn, but only from the surface.

Data are presented in table 2. This is a monofilament yarn (in the table coded as 196) prepared, wherein the yarn comprises 2 insecticides; herein piperonyl butoxide (first insecticide) and insecticide deltamethrin (second insecticide).

	SE1(mg/g)		SE2(mg/g)	
Sample code	Deltamethrin Yarn-1	Piperonyl butoxide Yarn-1	Deltamethrin Yarn-1	Piperonyl butoxide Yarn-1
196 replicate 1	0.0568	0.0210	0.0283	0.0398
196 replicate 2	0.0694	0.0204	0.0615	0.0492
196 average 1 and 2	**0.0631**	**0.0207**	**0.0449**	**0.0445**

Table 2. Piperonyl butoxide and deltamethrin present in the same yarn.
Sample 196 contains insecticide-1 herein piperonyl butoxide and insecticide- 2 herein deltamethrin and were present in the same yarn.

The data in table 2 shows that the concentration of piperonyl butoxide on the surface is higher (approximately 30% higher) from the beginning when present together with deltamethrin (Table 2) than when alone (Table 1). In the second extraction, piperonyl butoxide is again higher than in the first extraction. Opposite to that, Deltamethrin surface extraction has a lower value in the second extraction compared to that of the first extraction. It is concluded that the simultaneous presence of the two insecticides impact their surface concentrations and that the ratio of the two surface concentrations change from SE1 to SE2.

Data presented in table 3 show controlled release of both the insecticide deltamethrin and of piperonyl butoxide from monofilament yarn.

Sample code	SE1(mg/g)		SE2(mg/g)	
	Deltamethrin Yarn-1	Piperonyl butoxide Yarn-2	Deltamethrin Yarn-1	Piperonyl butoxide Yarn-2
197 replicate 1	0.0250	0.0100	0.0039	0.0382
197 replicate 2	0.0320	0.0136	0.0052	0.0370
197 average 1 and 2	**0.0285**	**0.0118**	**0.0045**	**0.0376**

Table 3. Sample 197 comprises two different yarns; one yarn comprising piperonyl butoxide and the other monofilament yarn deltamethrin.

Sample 197 comprises of two separate yarns; one with piperonyl butoxide and the other with deltamethrin that were thereafter are knitted together into a mosquito bednet. Example 4 describes the method of preparation of this sample. Each yarn is made with the same concentrations as in 195 and 196, therefore, when only half the yarns have each insecticide, the surface concentrations will be expected to be half of that found in 195 and 196.

Table 3 shows as before (table 2), that deltamethrin is lower in the second surface extraction than in the first and piperonyl butoxide is again higher in the second than in the first. The start values are around half t he values found in Table 1 and 2 as expected. It can be seen that it is not possible to use the same release composition for two different insecticides and with the described release composition one has an accelerated release and the other a decelerated release.

Thus, this type of textile product will not be as effective in the killing of insects as a product wherein yarn-1 (with insecticide-1) is releasing effective amounts in same speed as yarn-2 (insecticide-2).

It can be concluded that to obtain the effect that two insecticides are released percent wise equally, it is not possible to put them in the yarn and not possible to put them in two yarns with the same release composition.

Therefore, it is concluded that a release formulation must be optimized for each insecticide separately and the basic unit of the yarn (the filament) must be prepared and extruded separately. Each yarn has its unique release composition necessary to control speed and rate of release.

As understood by the skilled person – if the Confidence value is set at 90% - as described in example 3 - the slope of decay will be significantly different for the samples 195, 196 and 197.

Accordingly, samples 195, 196 and 197 will be outside the scope of the first aspect as described herein.

Example 5: *Deltamethrin present in two different yarns with different release composition (this example shows that the principle works and the skilled person can easily choose the different active ingredients to be incorporated)*

Release compositions are chosen specific for each insecticide to obtain equal release so that the life time of the product for both insecticides is the same

Sample 134 and 181 were prepared in the following way.

Preparation of samples

Sample code 134:
Hydroxy benzophenon: 4 %
Tinuvin 494: 7 % (commercially available from Ciba Geigy)
25 kg HDPE
23 g LLDPE (in the form of masterbatches)
2 kg MDPE+LDPE

Sample code 181
Hydroxy benzophenon: 4 %
Tinuvin 494: 7 % (commercially available from Ciba Geigy)
25 kg HDPE
3 kg LLDPE (in the form of masterbatches)

Sample code 134 and 181 contain the same additives used but are different in the polymer composition. The nets are washed in soap water according to WHO wash protocol (WHO: guidelines for laboratory and field testing of long lasting insecticidal mosquito nets; WHO/CDS/WHOPES/GCD PP/2005, further reference 4) after surface extraction 1 and surface extraction 2 and stored at 30°C for 4 days between washes.

Surface Deltamethrin is extracted with hexane (Cipac 331/LN/M/4).

Sample nr	Deltamethrin mg/g		
	SE 1	SE 2	SE 3
134	0.041	0.039	0.041
181	0.030	0.028	0.032

Table 4 tabulates the data collected for the two prepared samples coded 134 and 181. It is seen that for both products release rates are quite stable, but less is released from 181 than from 134.

These samples have also been analyzed in bioassays according to WHOPES I protocol (reference 4 herein).

Mortality

		0 washes		**1 wash**		**2 washes***		**5 washes***	
		N	% M	N	% M	N	% M	N	% M
P1 134	S1	50	100	47	100	50	100	55	100
	S2	50	100	43	100	50	100	58	100
P3 181	S1	50	100	50	92	48	81	53	9
	S2	50	100	54	93	50	76	49	12
Control	S1	51	0	92	0	105	0	46	0
		10 washes		**12 washes**		**15 washes**		**20 washes**	
		N	% M	N	% M	N	% M	N	% M
P1 134	S1	56	88	53	70	53	53	56	59
	S2								
P3 181	S1	56	19	61	4	61	9	54	22
	S2								
Control	S1	55	0	55	0	54	0	54	0

Table 5. Mortality of mosquitoes as measured in vivo assay as described in example 1 (killing of mosquitoes), measured at time 0 (no washes), after 1, 2 up to 20 washes. N is the amount of mosquitoes in the assay, S1 and S2, represent two separate replicates of sample code 134 or 181 and control is a textile sample without any insecticide. Details of the method are described in WHO 2005. For 134, Knock Down after 60 min remained near 100 % till 20 washes whereas it declined to an unstable level between 36 and 100 % for 181 after 5 washes.

Conclusion

It is concluded that the stable release rate measured for the two products after the initial washes (Table 4) did not remain stable up to 20 washes, but the surface concentration in

sample 134 was sufficiently high to kill more than 80 % up to 10 washes and have a knock down near 100 % until 20 washes.

Contrary to that, the surface concentration in sample P181 was not sufficiently high to provide an effective product as defined by WHO (2005, reference 4). Mortality declined below 80 % before 5 washes and knock down was too low. It can thus be seen that the polymer composition can be used to obtain a sufficient release rate of deltamethrin over 20 washes, whereas the same additive composition with another polymer composition gives an inefficient product. It is possible to adjust release rate of an insecticide by changing the polymer composition. When two different insecticides are used, two different polymer compositions can thus be used to regulate surface concentration and thereby release rates.

REFERENCES

1. Cédric Pennetier et al., Malaria Journal March 2007, (6):38

2. P. Guillet et al; Medical and Veterinary Entomology 15 (1): 105–112

3. Pennetier et al Am. J. Trop. Med. Hygiene 2005 June; 72 (6): 739-744.

4. WHO: guidelines for laboratory and field testing of long lasting insecticidal mosquito nets; WHO/CDS/WHOPES/GCD PP/2005 guidelines.

5. WO00137662

6. WO2007085640

CLAIMS

1. A textile product to kill insects,

(1a): wherein the textile comprises at least two different yarn types characterized by that:
the first yarn type releases at least one active ingredient selected from the group consisting of an insecticide and the second yarn type releases at least one active ingredient, but not the same as the first yarn, selected from the group consisting of an insecticide, an insect repellent, pesticide synergist and a chemosterilant;
or

(1b): wherein the textile comprises a yarn comprising at least two different filament types spun into the yarn characterized by that:
the first filament type releases at least one active ingredient selected from the group consisting of an insecticide and the second filament type releases at least one active ingredient, but not the same as the first filament type, selected from the group consisting of an insecticide, an insect repellent, pesticide synergist and a chemosterilant;

and wherein

(a): the two different active ingredients are both present on the surface of the yarn after 20 defined laboratory washes as described in WHO: guidelines for laboratory and field testing of long lasting insecticidal mosquito nets; WHO/CDS/WHOPES/GCD PP/2005 guidelines; and

(b): the release rate of the two different active ingredients are essentially the same for both, as measured by determining the slope of the decay as described in example 3 and where the slope of decay for the two different active ingredients may not be significantly different, defined as the confidence is at least 90%.

2. The textile product of claims 1, wherein the polymer in the first yarn or filament type is different from the polymer of the second yarn or filament type due to they have different chain lengths and branching to obtain different density and crystalline structure and thus different glass points.

3. The textile product of claim 1, wherein the product is a product selected from the group consisting of net, mosquito bednet, curtain, cushion, wall covering textile, tarpaulin, cloths and window/door screen.

4. The textile product of claim 3, wherein the product is a mosquito bednet.

5. The textile product of any of the preceding claims, wherein the two different yarn or filament types both comprise at least one polymer selected from the group consisting of: polyester, polyethylene, polypropylene, polyacrylic and polyurethane; and wherein the polymers are different in the two different yarn or filament types.

6. The textile product of claim 5, wherein the polymers of the first yarn or filament type are comprising approximately equal amounts of high density polyethylene (HDPE) and linear low-density polyethylene (LLDPE); and the polymers of the second yarn or filament type are comprising at least 6 times more of high density polyethylene (HDPE) than linear low-density polyethylene (LLDPE).

7. The textile product of any of the preceding claims, wherein the insecticide is at least one insecticide selected from the group consisting of pyrethroids, organophosphates and carbamates.

8. The textile product of claim 7, wherein the second yarn or filament type releases at least one pesticide synergist, such as e.g. piperonyl butoxide.

9. The textile product of claim 7, the first yarn or filament type releases at least one pyrethroid and the second yarn or filament type releases at least one carbamate.

10. The textile product of claim 7 to 9, wherein the pyrethroid is deltamethrin or permethrin.

11. The textile product of any of the preceding claims, wherein the Confidence of point (b) of claim 1 is at least 95%.

12. A textile product to kill insects of any of claim 1 to 11, wherein the textile product is obtainable by a method of any of claims 14 or 16.

13. The textile product to kill insects of claim 12, wherein the textile product is obtainable by a method of claims 15 or 16.

14. A method to manufacture a textile product of claim 1 comprising the following steps:
(Ia): making a first yarn type that release at least one active ingredient selected from the group consisting of an insecticide and a second yarn type that release at least one active ingredient, but not the same as the first yarn, selected from the group consisting of an insecticide, an insect repellent and a chemosterilant;

or

(Ib): making a yarn comprising at least two different filament types spun into the yarn characterized

by that:

(i): the first filament type releases at least one active ingredient selected from the group consisting of an insecticide and the second filament type releases at least one active ingredient, but not the same as the first filament type, selected from the group consisting of an insecticide, an insect repellent and a chemosterilant;

and

(IIa): weaving or knitting parts of the textile product comprising the first type of yarn with one active ingredient and other parts with the second type of yarn com-prising another different active ingredient (in case of step Ia) ;

or

(IIb) weaving or knitting the textile product by mixing the yarn types (in case of step Ia) or the yarn type (in case of step IIb) randomly in all relevant parts of the textile product;

and

(III) cut the textile product and shape it into a bednet, tarpaulin or any given shape fitting the end use.

15. The method of claim 14, wherein there is used option (IIb) in step (II).

16. The method of claim 14, wherein the textile product comprises at least 50% of such randomly woven or knitted part.

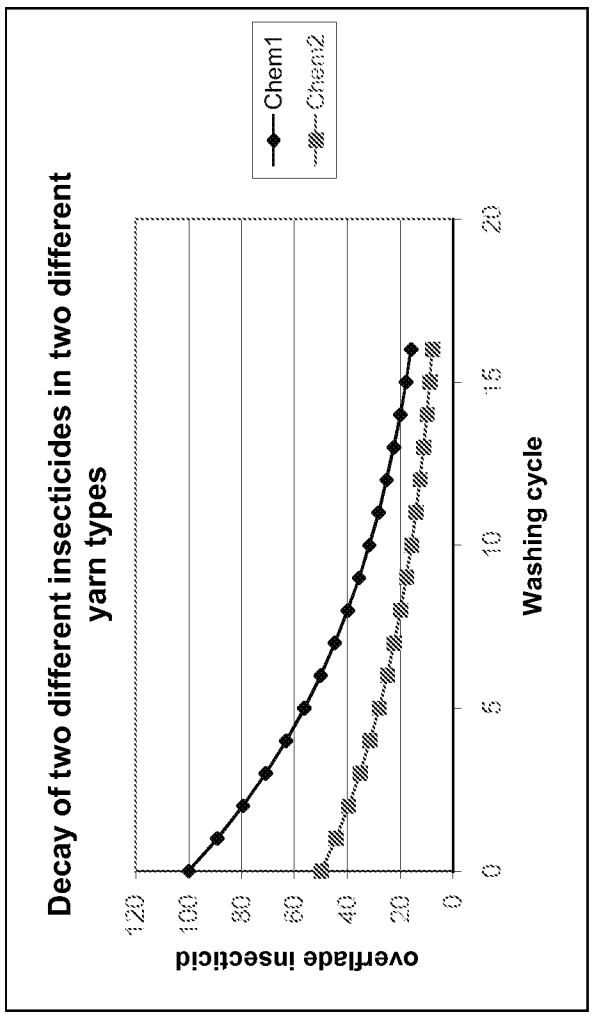

Figure 1: Graphical (linear) presentation of two insecticides with each its decay levels in the time.

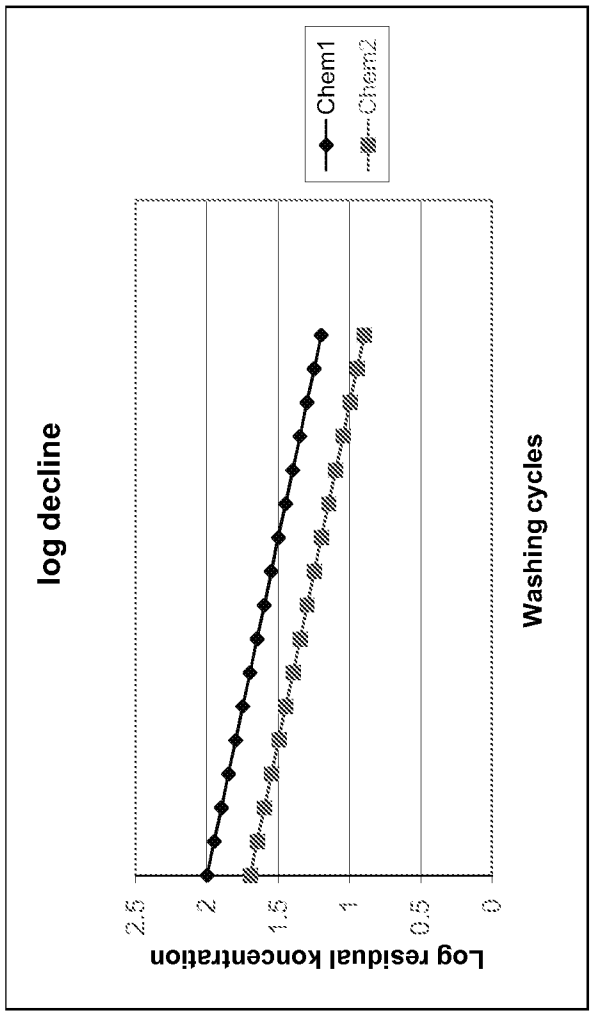

Figure 2: Logarithmic transformation of the linear data of decay of 2 insecticides in two different yarns.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2009/063688

A. CLASSIFICATION OF SUBJECT MATTER
INV. D01F1/10 D01F6/46 A01N25/34 D02G3/04 D03D15/00

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
D01F A01N D02G D03D

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	US 5 801 194 A (VORIS PETER VAN [US] ET AL) 1 September 1998 (1998-09-01) column 10, line 40 - column 11, line 42 figure 20 claims 1,4	1-5,7, 10-11 6,8-9
Y	JP 08 302080 A (FUKUVI CHEM IND CO) 19 November 1996 (1996-11-19) abstract	6
Y	WO 2008/098572 A1 (DISEASE CONTROL TEXTILES SA [CH]; FRANDSEN MIKKEL VESTERGAARD [CH]) 21 August 2008 (2008-08-21) page 4, line 7 - page 5, line 3	8-9

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
15 March 2010	22/03/2010

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2009/063688

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	WO 2009/003468 A1 (VESTERGAARD FRANDSEN SA [CH]; VESTERGAARD FRANDSEN MIKKEL [CH]) 8 January 2009 (2009-01-08) page 3, line 4 - line 15 claims figures 1,3,6	1-5,7-16
X,P	WO 2009/059607 A2 (VESTERGAARD FRANDSEN SA [CH]; VESTERGAARD FRANDSEN MIKKEL [CH]) 14 May 2009 (2009-05-14) page 12, line 29 - page 13, line 13	1-5, 7-14,16
A	JP 08 120551 A (KOMATSU FELT SEIZOSHO KK) 14 May 1996 (1996-05-14) abstract claims 4,8,9 example	1-16

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2009/063688

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5801194 A	01-09-1998	NONE	
JP 8302080 A	19-11-1996	JP 3535258 B2	07-06-2004
WO 2008098572 A1	21-08-2008	CN 101616582 A	30-12-2009
WO 2009003468 A1	08-01-2009	NONE	
WO 2009059607 A2	14-05-2009	WO 2009059603 A1	14-05-2009
JP 8120551 A	14-05-1996	NONE	