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(54) **SOLUBLE SACHET FOR WATER-BASED COMPOSITIONS**

LÖSLICHER BEUTEL FÜR WASSERHALTIGE SUBSTANZEN

SACHET SOLUBLE POUR COMPOSITIONS AQUEUSES

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(56) References cited:
**EP-A- 0 079 248 EP-A- 0 341 188
US-A- 4 348 293**

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Description

[0001] The present invention relates to a (preferably cold) water-soluble sachet having packaged therein a water-based composition, such as a water-based agrochemical, laundry care, dyestuff, biocide, industrial or home surface cleaning, or public health material composition.

[0002] Water-soluble sachets have utility for packaging a range of materials, usually formulated compositions, and particularly formulated compositions which are hazardous (or at any rate unpleasant) to individuals with whom they come into contact or are hazardous or harmful to the environment. Important examples include agrochemicals compositions (e.g. insecticides, herbicides, pesticides and fungicides), laundry care products (e.g. detergents, fabric softeners and bleaches), dyestuffs, biocides, industrial or home cleaners, and public health products. The use of water-soluble sachets for packaging certain formulated compositions also provides a convenient way of adding a measured dosage of the formulation for subsequent dilution with water in order to provide the desired final concentration of the diluted formulation.

[0003] Agrochemical compositions for example can be packaged in water-soluble sachets, in which form they can be safely handled. The water-soluble sachet can be subsequently added to a spray tank containing water, and after dissolution of the sachet, the diluted formulation can be sprayed by the user, e.g. by a farmer. Complete dissolution or disintegration of the sachet is normally necessary to avoid blockages during the spraying operation. It is therefore usually desirable that the film is cold water-soluble since it would be difficult to employ hot water in large scale outdoor use. Cold water-soluble means herein soluble in water at temperatures $\leq 35^{\circ}\text{C}$, and generally between 5 and 35°C .

[0004] Polyvinyl alcohol is widely utilised for the preparation of water-soluble film for the production of sachets for packaging materials of the type discussed above (such as agrochemicals); polyethylene oxide and methyl cellulose are also widely utilised (see e.g. WO 93/22215). Such polymers are normally used in conjunction with a plasticiser to achieve the desired level of flexibility in the sachet film. Other types of polymers which are useful for providing films for sachet construction include acrylic polymers bearing neutralised acid groups (particularly carboxyl groups), the latter providing the requisite water-solubility for the acrylic films derived from the polymers.

[0005] The packaged material in a sachet is often in the form of a water-based composition, by which is meant that the active material(s) of the composition, optionally with other components which may also be present in the composition, are carried in a liquid medium the principal component of which is water. Preferably at least 60 wt% of the liquid carrier medium is water, more preferably at least 70 wt% (the non-aqueous component of the liquid carrier medium, if any, normally being one or more organic liquids). The aqueous composition may e.g. be in the form of an aqueous solution or an aqueous dispersion (such as a suspension concentrate or an oil-in-water emulsion) of the component(s) thereof.

[0006] For example a type of laundry care sachet is proposed in European Patent Application EP-A-O 079 248, where a water-soluble film is coated with a protective layer of particulate inert plastics material. The protective layer, when on the inside of the sachet protects the water-soluble film from attack from aqueous media.

[0007] In International Patent Application WO97/27743 a water-soluble sachet for packaging aqueous media based agrochemical compositions is proposed. Instead of an internal protective layer, an agent to minimise water loss is provided as part of the composition.

[0008] While it is a primary objective that the aqueous-based composition of the sachet should be releasable into the selected aqueous environment at the appropriate time and place, by virtue of the sachet film(s) becoming dissolved and/or disintegrating in the water, (for the purpose of this specification, "water-soluble" includes "water-disintegratable"). There is a recognised problem that the water of the aqueous-based composition of the sachet may in certain circumstances and for some compositions permeate through the sachet wall prior to use, e.g. during storage. Such permeation of the water of the packaged composition is clearly highly undesirable and may e.g. cause the sachet to dissolve and adhere to outer packaging thereby reducing the shelf life of the packaged product.

[0009] We have now discovered how to overcome the problem of permeation when aqueous-based compositions are packaged in water-soluble sachets.

[0010] According to the present invention there is provided a water-soluble sachet suitable for packaging a water-based composition, the sachet having a film construction comprising a water-soluble film the binder material of which comprises a water-soluble organic polymer(s), and which film construction incorporates a water-dispersible wax(es) derived from an aqueous dispersion of the wax(es) employed in the formation of the water-soluble film.

[0011] In an alternative embodiment of the present invention there is provided the combination of a water-soluble sachet and a water-based composition packaged therein, the sachet having a film construction comprising a water-soluble film the binder material of which comprises a water-soluble organic polymer(s), and which film construction incorporates a water-dispersible wax(es) derived from an aqueous dispersion of the wax(es) employed in the formation of the water-soluble film.

[0012] There is further provided according to the invention a water-soluble sachet, in fully or partially sealed form, for packaging a water-based composition, said sachet having a film construction as defined above.

[0013] There is further provided according to the invention a method of making a sachet as defined above which method comprises preparing a water-soluble film from an aqueous solution or dispersion of a water-soluble organic polymer(s) in admixture with an aqueous dispersion of a wax(es) and forming a sachet whose film construction comprises said water-soluble film.

[0014] It has thus been found that the presence of the wax component in the water-soluble film construction of the sachet, which has been introduced as defined above, significantly reduces or prevents permeation of the aqueous contents of the sachet. It is believed that the wax migrates to the surface of the film, thus providing a wax layer which reduces or prevents permeation of the water of the aqueous formulation through the film. However, we would not wish to be bound by this possible explanation.

[0015] The term "wax" is used to generically classify many materials that are either natural or synthetic, and of petroleum, mineral, vegetable, or animal origin. They are normally solid at ambient temperature with a relatively low melting point, and capable of softening when heated and hardening when cooled (e.g. having a melting point of $\geq 50^{\circ}\text{C}$, and usually within the range of 50 to 90°C). They are themselves insoluble in water. Waxes obtained from natural sources include animal waxes, vegetable waxes, mineral waxes and petroleum waxes. Examples of such materials, which may often be used in combination, include petroleum waxes such as paraffin waxes of various melting points and grades and microcrystalline wax; animal waxes such as beeswax; vegetable waxes such as carnuba wax and candelilla wax; and mineral waxes such as maston wax.

[0016] The wax(es) to be used in the invention should be water-dispersible, i.e. capable of being dispersed into water using e.g. surfactant(s) and high energy agitation. Such aqueous dispersions of waxes are usually available commercially, and are known as aqueous wax emulsions. Particularly preferred waxes are paraffin waxes (i.e. hydrocarbon or hydrocarbon-mixture waxes) and carnuba wax (often being used in combination). Thus a commercially available aqueous wax emulsion of this type is "Michelman" ML270-E which is an aqueous wax emulsion (average particle size of about $1\mu\text{m}$) of a mixture of paraffin and carnuba waxes, often delivered at about 40% w/w solids. The wax emulsion may be diluted with water if necessary before use in the invention.

[0017] The aqueous wax emulsion is employed as a means for incorporating the wax(es) into the water-soluble film construction of the sachet.

[0018] Preferably this is effected by admixture of an aqueous solution or dispersion (usually latex) of a water-soluble organic polymer(s) to be used as a film-forming binder(s) for the sachet with an aqueous emulsion of the wax(es). (If the film-forming polymeric binder is in dispersion (e.g. latex) form at this stage, it should be capable of being converted to an aqueous solution at a subsequent stage, e.g. by bearing sufficient acid groups if an acrylic polymer, usually carboxylic acid groups, which will provide water-solubility by neutralisation with a base). Usually this admixture will be a simple admixture, although an in-situ polymerisation to form a water-soluble polymer in the presence of an aqueous wax dispersion is not in principle discounted.

[0019] The aqueous wax emulsion which is admixed with the aqueous solution (or dispersion) of the water-soluble film-forming polymer (as mentioned above), in a further embodiment of the invention is already in admixture with an acrylic polymer latex, usually in a wax/acrylic polymer weight ratio within the range of 99/1 to 50/50 (more preferably 90/10 to 70/30). This acrylic polymer may itself be water-soluble, e.g. by bearing neutralizable acid groups (usually carboxyl) at a sufficiently high level such that the polymer can subsequently become solubilized if desired by appropriate neutralisation with a base. On the other hand this acrylic polymer need not be water-insoluble, e.g. by not being neutralised (if it bears acid groups) or by being inherently hydrophobic (e.g. by not bearing any or insufficient acid groups) so that it is water-insoluble at any pH. In such combinations of wax emulsion and water-insoluble acrylic polymer used for this embodiment (i.e. which is then admixed with the water-soluble film-forming polymer), the acrylic polymer may have a glass transition temperature (T_g) ranging from -20°C to 100°C , more preferably 10 to 50°C .

[0020] The utility of this further embodiment is to further upgrade the quality of the water-soluble film of the sachet e.g. by improving its blocking resistance, improving film flexibility under low humidity conditions, and increasing solubility in cold water (when the further polymer is itself water-soluble). Usually the acrylic polymer latex that is already in admixture with the wax emulsion before admixture with the water-soluble polymer(s) to be used as the film forming binder(s) for the sachet is present in small amount compared to the weight of the water-soluble film-forming polymer binder(s) itself. Preferably the acrylic polymer (in admixture with the wax) in this embodiment is present in an amount of 0.01 to 30 wt.%, more preferably 0.3 to 5 wt %, based on the weight of the water-soluble organic polymer(s) used as the film-forming binder(s) of the sachet.

[0021] Returning to the water-soluble organic polymer(s) which is used as the film-forming binder(s) to provide the water-soluble film construction of the sachet. Examples of such polymers include polyethylene oxide, methyl cellulose and, especially, polyvinylalcohol (PVOH). The PVOH is generally partially or fully alcoholysed or hydrolysed, for example 40-100%, especially 80-100% (and often specifically 88%), alcoholysed or hydrolysed polyvinyl acetate. The resulting PVOH film may be a laminate of two or more thicknesses of film, a surface modified film or a co-extruded film. PVOH films include M7030 (a monolayer film), L7030 (a laminate film), M7031 (a monolayer film), L7031 (a laminate film) and M9500 (also referred to as PXP2841, a monolayer film) all available from Chris Craft Industrial Products

Inc. of-South Holland, Illinois, USA.

[0022] Other suitable polymers for this purpose include, in particular (as mentioned above), acrylic polymers bearing sufficient acid groups (usually carboxyl groups) for rendering the polymer water-soluble on neutralisation with a base. Usually such polymers are made from a monomer charge containing 5 to 40 wt %, more usually 8 to 15 wt % of olefinically unsaturated carboxylic acid-bearing monomer(s) (examples of such carboxylic acid-bearing monomers being acrylic acid, methacrylic acid, β -carboxyethyl acrylate, maleic acid, and maleic anhydride), 40 to 95 wt%, more preferably 75 to 90 wt % of non-acid (meth)acrylate ester monomers containing 1 to 12 carbon atoms in the alcoholic ester-forming moiety, preferably C1 - C10 alkyl or hydroxyalkyl acrylates or methacrylates (examples of such monomers being methyl methacrylate, ethyl acrylate, n-butyl acrylate, 2-ethylhexyl acrylate, ethyl methacrylate, n-butyl methacrylate, hydroxyethyl acrylate, and hydroxyethyl methacrylate), and 0 to 20 wt%, more preferably 2 to 10 wt % of olefinically unsaturated monomers other than those mentioned above (examples of such further monomers being styrene, acrylamide, methacrylamide, 2-acrylamidomethylpropane sulphonic acid, and behenyl ethoxy(25) methacrylate).

[0023] A particularly preferred water-soluble acrylic polymer system for providing the water-soluble film-forming binder of the sachet is described in pending PCT International Application WO 97/00282. This discloses an acrylic polymer combination suitable for the provision of a flexible, water-soluble (preferably cold water-soluble), substantially or wholly plasticiser-free film which is itself suitable for the provision of the enveloping material of a sachet, said polymer system comprising a combination of the polymer components S and H, where

S is defined as at least one acid-functional addition copolymer which is soft in character by virtue of having a $T_g \leq 20^\circ\text{C}$, and

H is defined as at least one acid-functional addition copolymer which is hard in character by virtue of having a $T_g \geq 40^\circ\text{C}$,

and wherein further the components S and H are present in a relative weight ratio of S to H within the range of from 90/10 to 65/35 and the acid-functionalities of S and H are at least partly neutralised such as to render the resulting film water-soluble.

[0024] By the T_g of a copolymer herein is meant the glass transition temperature of the copolymer; as is well known, the T_g of a polymer is the temperature at which it changes from a glassy, brittle state to a plastic, rubbery state. T_g may be determined experimentally, e.g. by using differential scanning calorimetry (DSC), taking the peak of the derivative curve as T_g , or calculated from the well known Fox equation.

[0025] A copolymer of type S will often be derived from monomers comprising the following amounts (based on the total weight of monomers used) of acid-functional monomer(s), soft monomer(s), and hard monomer(s):

acid-functional monomer(s)	5 to 40 wt.%, more usually 8 to 15 wt.%, particularly 8 to 14 wt.%.
soft monomer(s)	40 to 85 wt.%, more usually 55 to 70 wt.%, particularly 60 to 70 wt.%.
hard monomer(s)	5 to 50 wt.%, more usually 15 to 35 wt.%, particularly 20 to 30 wt.%.

[0026] (The above amounts of soft and hard monomers exclude acid-functional monomers whether hard or soft : these are included in the acid-functional monomer range).

[0027] Examples of monomers combinations for making the soft copolymers (using appropriate levels of soft and hard monomers) are : acrylic acid/ethyl acrylate/methyl methacrylate; acrylic acid/n-butyl acrylate/ethyl acrylate/methyl methacrylate; acrylic acid/n-butyl acrylate/methyl methacrylate; methacrylic acid/ethyl acrylate/n-butylacrylate/methyl methacrylate; acrylic acid/methacrylic acid/n-butyl acrylate/ethyl acrylate/methyl methacrylate; and acrylic acid/methacrylic acid/ethyl acrylate/methyl methacrylate.

[0028] Examples of suitable soft and hard monomers for copolymers of type H are as described supra in respect of the soft and hard monomers for copolymers of type S.

[0029] A copolymer of type H will often be derived from monomers comprising the following amounts (based on the total weight of monomers used) of acid functional monomer(s), soft monomer(s), and hard monomer(s):

acid-functional monomer(s)	5 to 40 wt.%, more usually 8 to 15 wt.%, particularly 8 to 14 wt.%.
soft monomer(s)	0 to 50 wt.%, more usually 10 to 40 wt.%, particularly 25 to 40 wt.%.

(continued)

hard monomer(s)	40 to 90 wt.%, more usually 50 to 80 wt.%, particularly 50 to 65 wt.%.
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[0030] (The above levels of soft and hard monomers exclude acid-functional monomers whether hard or soft : these are included in the acid-functional monomer range).

[0031] Examples of monomer combinations for making the hard copolymers can be the same as those described supra for soft copolymers, but of course using different (i.e. appropriate) amounts of hard and soft monomers.

[0032] With regard to the neutralisation of the acid-functional groups in acrylic polymers (where this is required to achieve water solubility), the required degree of neutralisation can be brought about by the use of an appropriate base or basic salt so as to convert the desired proportion of acid-functional groups to anionic salt groups together with the corresponding presence of cations derived from the base of basic salt. Bases which could be used are non-volatile (i.e. permanent) bases such as the Group IA or II metal bases or basic salts, e.g. hydroxides, bicarbonates or carbonates (as appropriate) and particularly the hydroxides of Na, K and Li, and non-volatile water-soluble organic bases such as triethanolamine and 2-methyl-2-amino-1-propanol. Volatile bases which could be used are ammonia and volatile aliphatic amines such as triethylamine, diethanolamine and the like. However, it is preferred in most cases to use non-volatile (i.e. permanent or fixed) bases (since volatile bases might be lost during film formation and storage of the films - leading to impaired water-solubility), with the most preferred permanent base being NaOH. Nevertheless, the use of volatile bases such as (in particular) ammonia may be advantageous in some cases.

[0033] Water-soluble acrylic polymers, including acrylic polymer combinations, as with PVOH polymers discussed above, may provide resulting sachet film constructions of the monolayer type or the laminate type. It would also be possible in principle to employ a laminate construction of two quite different polymer types, e.g. a PVOH film laminated with an acrylic film.

[0034] In the case of employing a laminate structure for the resulting sachet, the wax may be incorporated into one or both of the laminate films. If incorporated into only one film, it is usually incorporated in the outer layer of the resulting sachet, although incorporation into only the inner layer is also possible.

[0035] In principle, any technique may be used to make a water-soluble film as described above, for example calendering, extrusion or, more preferably, casting. When the film is to be made by casting, a solution or dispersion of the polymer system, together with any desired additive(s) (e.g. the wax), could e.g. be poured onto a suitable mould flat horizontal surface (e.g. made of a plastics material such as polyethylene or polypropylene) and the aqueous carrier phase removed by natural or accelerated evaporation (e.g. at room temperature or at an elevated temperature as for example in an oven). A film could also be made by coating onto a flat surface using an applicator bar to determine film thickness rather than mould dimensions. Laminate films may be formed by techniques such as sequential casting, co-extrusion, and lamination of two preformed films.

[0036] The sachet film is preferably self-supporting.

[0037] A wax-containing water-soluble film, whether in monolayer or laminate form, which is used for the film construction of an invention sachet should preferably contain from 1 to 30 wt.%, more preferably 3 to 10 wt.% of wax, based on the total dry weight of the film (and as mentioned above, in the case of a laminate film, the wax may be present in one or both of the two films and usually in at least the outer film).

[0038] The water-soluble film used for making the invention sachet may also include (besides wax) if desired materials such as slip aids, colourants, wetting agents (surfactants), fillers (e.g. silica or starch), chelating agents, and (where necessary) plasticisers (such as glycerol e.g. in the case of polyvinyl alcohol film).

[0039] The aqueous-based composition packaged in the water-soluble sachet is, in particular, an agrochemical composition comprising a water-soluble, agrochemically active ingredient, water, and optionally other components, such as electrolytes, thickeners, chelating agents, antifreeze-agents, antifoam agents, buffers, dyes, emetics, preservatives, odourants, perfumes, safeners, organic solvents, stabilisers, synergists and wetting agents.

[0040] The water-soluble agrochemically active ingredient, is, for example, a herbicide such as a paraquat salt (for example paraquat dichloride or paraquat bis(methylsulphate)), a diquat salt (for example diquat dibromide or diquat alginate) or glyphosate or a salt or ester thereof (such as glyphosate isopropylammonium, glyphosate sesquisodium or glyphosate trimesium (also known as sulfosate)), an insecticide or a fungicide. It is preferred that the water-soluble agrochemical is paraquat dichloride, diquat dibromide, glyphosate isopropylammonium or glyphosate trimesium (also known as sulfosate).

[0041] An electrolyte can be included in to the composition to increase its ionic strength. The electrolyte concentration in the aqueous composition may be greater than the electrolyte concentration in the water in which the sachet is to be dissolved. The electrolyte normally would help to improve the insolubility of the material from which the sachet is made in the composition. Preferred electrolytes are ammonium sulphate, sodium sulphate, potassium sulphate, copper sulphate, ammonium nitrate, sodium nitrate, magnesium sulphate, potassium nitrate, sodium chloride and potassium

chloride.

[0042] Adjuvants or co-formulants (such as wetters or anti-freezing agents) may also be comprised in the composition. Suitable adjuvants include neutral or anionic surfactants [such as a soap, a salt of an aliphatic monoester of sulphuric acid (for example, sodium lauryl sulphate), a salt of a sulphonated aromatic compound (for example, sodium dodecylbenzenesulphonate) or an alkyl glucoside] or polysaccharides. Suitable wetters include an alkyl glycoside, a salt of a sulphonated aromatic compound (for example, sodium dodecylbenzenesulphonate), an alcohol ethoxylate or a diglucamide. Suitable thickeners include various grades of xanthan gum.

[0043] The agrochemical composition may also comprise a chelating or sequestering agent for calcium ions. A suitable chelating or sequestering agent is ethylenediaminetetraacetic acid.

[0044] Additionally the agrochemical composition may also comprise an adhesive, an antifoaming agent, a buffer, a deodorant, a dye, an emetic, a preservative, an odourant, a perfume, a safener, a further solvent, a stabiliser, a synergist, a thickener or a wetting agent.

[0045] The water-soluble sachet can be formed and filled using standard techniques (such as thermoforming or vertical form-fill-sealing).

[0046] In use, the packaged agrochemical composition is mixed with water (for example in an agrochemical sprayer) to give a sprayable solution of the water-soluble agrochemically active ingredient.

[0047] A packaged aqueous-based composition (in particular a packaged aqueous agrochemical composition) of the present invention can be part of a bag-in-bag arrangement (for example an arrangement wherein the packaged aqueous-based composition of the present invention is enclosed within a second water-soluble sachet holding only the packaged aqueous-based composition of the present invention [the second sachet presenting a further barrier to contain the agrochemical composition]), part of an arrangement where two water-soluble sachets are joined at a common seal or part of an arrangement where seals of two water-soluble sachets are joined by a hinge of water-soluble film.

[0048] It is also possible for invention water-soluble sachets to be packaged in a non water-soluble outer bag acting as secondary packaging (e.g. made from a polyethylene/aluminium foil/paper laminate).

[0049] The present invention is now illustrated by reference to the following examples. Unless otherwise specified all parts, percentages and ratios are on a weight basis.

[0050] In the examples, the following abbreviations are used:

PVOH	polyvinyl alcohol
DFT	dry film thickness

Preparation of PVOH Solutions

[0051] Aqueous PVOH solutions were prepared for example as follows:

[0052] A solution in water at 15% w/w active component was prepared where the active component is:

PVOH	77.8%
Glycerol	15.6% (plasticiser)
Starch	6.6% (filler)

PVOH =	'Mowiol 40-88', 88% hydrolysed, M. Wt. 127K, ex- Aldrich
Glycerol =	Glycerol analar, ex-BDH
Starch =	'Avedex 36LAC14U', ex-Avebe Ltd

Example:

[0053] Distilled water (340g) was stirred in a flask at room temperature. To this was added glycerol (9.36g), starch (3.96g) and PVOH (46.68g). The mixture was heated to 80°C and stirred continuously until the PVOH completely dissolved. The PVOH solution was then allowed to cool to room temperature without stirring to allow for removal of entrapped air.

Preparation of PVOH/Wax Solutions

[0054] Aqueous solutions of PVOH/wax were prepared for example as follows:

[0055] To obtain films of DFT of about 80µm, two coats are cast each of about 40µm DFT. When a wax containing

film containing 10% w/w wax is required, on total film weight, the wax is combined in the second coat only at a level of 20% w/w.

[0056] The wax emulsion is reduced to 15% w/w solids content by dilution with water. This is then added to the above PVOH solution with stirring at room temperature.

Example:

[0057] To produce a final film composition containing 8.3% w/w wax a PVOH/wax formulation is prepared containing 16.6% w/w wax. To 15g of 'Michelman ML270-E' wax emulsion (mixture of paraffin and carnuba waxes, delivered as 40% w/w solids) was added 25g of distilled water, so yielding a wax emulsion at 15% w/w solids. PVOH solution (200g; 15% solids) was stirred at room temperature and the diluted wax emulsion (40g) was added over 10 minutes to give the desired formulation containing 16.6% w/w wax. The wax emulsion can also be added to PVOH solution and stirred at 80°C as well as at ambient temperature).

Preparation of Water-Soluble Films for Sachets

[0058] Films of about 80µm DFT were made for the construction of these sachets. This was achieved by casting 2 layers of formulation, each being of about 40µm DFT. The first coat was allowed to dry before application of the second coat.

Example:

[0059] Production of a film laminate containing 8.3% w/w wax was prepared as follows. Firstly, a layer of a PVOH solution (in the absence of wax) was cast on untreated polypropylene sheet using a sheen Micrometer Adjustable Film Applicator to give a wet film thickness of 270µm. This film was dried at 80°C for 1 hour. Then a second coat of the PVOH/wax formulation (16.6% w/w wax) was applied on top of the first coat (wet film thickness of 270µm). This was again dried at 80°C for 1 hour. A final laminate coating was obtained at about 80µm DFT containing 8.3% w/w wax, in which the contained wax is believed to-have stratified to the coating/air interface during drying.

Construction and Filling of Water-Soluble Sachets

[0060] The prepared films on polypropylene were cut to 240mm x 200mm. The polypropylene backing was then carefully removed. The film was folded in half lengthways. The wax-containing film formed the outer film of the sachet. The 2 shorter sides of the sachet were heat-sealed using a Hulme-Martin heat sealer. For PVOH-based films the heat setting was 6.5 and the cool setting was 8.5. The resulting sachet had the fold as the bottom edge. The sachet was filled with 70ml of saturated magnesium sulphate. The final side was then heat-sealed. This gives a sachet of approximate dimensions of 200mm x 120mm.

Construction of Outer Bags

[0061] The above water soluble sachets were contained in secondary outer packaging for storage; a laminate of polythene/aluminium foil/paper (90 micron DFT) was prepared with the polythene forming the inner side of the resulting package. Sheets of this material were cut to 210mm x 200mm. Two such sheets were placed together on top of each other and three sides heat-sealed. A water-soluble sachet was then placed inside this outer packing and the final side of the outer packing was heat-sealed.

Testing

[0062] A series of water-soluble films, with and without outer packaging, were subjected to storage trials at 40°C and 40% relative humidity. The loss of water from the aqueous contents was determined gravimetrically. Further, the dissolution rates of the water soluble films were determined, both prior to and after storage.

ResultsStorage TrialsExample 1 : Water Soluble Sachets with No Outer Packaging

[0063] Four films were studied, each in duplicate;

- 1a PVOH with no wax
- 1b PVOH + 2.49% w/w wax
- 1c PVOH + 4.15% w/w wax
- 1d PVOH + 8.3% w/w wax

[0064] These sachets were stored for 3 days before determining water loss. Due to the absence of outer packaging water loss from the sachets is considerable under the conditions of storage; after 3 days, precipitation of magnesium sulphate was observed and results after this time were considered to be unreliable. The results demonstrate the basic influence of the wax's ability to reduce water loss, particularly at the 8.3% w/w level.

Example No.	Replicate No.	Initial Weight (g)	Final Weight (g)	Weight Loss (%)
1a	1	95.95	72.11	24.85
1a	2	95.25	71.21	25.24
1b	1	95.44	72.83	23.69
1b	2	94.64	73.07	22.79
1c	1	97.10	76.12	21.61
1c	2	94.75	73.39	22.54
1d	1	97.42	80.46	17.41
1d	2	96.08	79.56	17.19

Example 2 : Water Soluble Sachets Contained in Outer Packaging

[0065] Three films were studied, each in duplicate

- 2a PVOH
- 2b PVOH + 4.15% wax
- 2c PVOH + 8.3% wax

[0066] These sachets were stored for 4 weeks before determining weight loss.

Example No.	Replicate No.	Initial Weight (g)	Final Weight (g)	Weight Loss (%)
2a	1	95.23	93.88	1.42
2a	2	96.81	95.39	1.47
2b	1	96.18	95.46	0.75
2b	2	95.90	95.12	0.81
2c	1	96.45	95.92	0.55
2c	2	95.07	94.59	0.50

[0067] This set of results clearly shows a 46% reduction in the water loss from the contents as a consequence of incorporating 4.15% w/w wax in the film composition, and a 63% reduction in water loss when 8.3% wax is incorporated in the film composition.

General Test for Testing the Solubility of Films in Water

[0068] The solubility of the films was determined by mounting the film in a 35mm slide frame and immersing the slide mount into 500 cm³ of water (distilled or tap), in a 600 cm³ beaker, maintained at 10°C. The slide mount is stirred at 400 rpm using a 2.5cm length magnetic stirrer bar.

[0069] The breakthrough time was defined as the time taken for the film sample to break free of the slide frame and dissolution time was measured as the time taken for complete dissolution of the film such that no trace of film remained when filtered through a 150 micron mesh sieve.

Film 80µm DFT	Film Break-Through (seconds)	Film Dissolution (minutes)
PVOH	90	6.5
PVOH + 2.49% wax	120	9.5
PVOH + 4.15% wax	120	14
PVOH + 8.3% wax	75	21

[0070] Addition of wax thus had negligible effect on the film rupture time though there was an increase in the time required for complete dissolution.

[0071] Upon dissolution the wax re-disperses reverting back to an aqueous emulsion form of low enough particle size so as not to block the sieve.

[0072] If the dissolution time is greater than 60 minutes then the film is considered insoluble for this purpose.

Claims

1. Water-soluble sachet suitable for packaging a water-based composition, the sachet having a film construction comprising a water-soluble film the binder material of which comprises a water-soluble organic polymer(s), and which film construction incorporates a water-dispersible wax(es) derived from an aqueous dispersion of the wax (es) employed in the formation of the water-soluble film.

2. Sachet according to claim 1 wherein the water-based composition is a water-based agrochemical, laundry care, dyestuff, biocide, industrial cleaning, home surface cleaning or a public health material composition.

3. Sachet according to claim 2 wherein the water-based composition is an agrochemical composition, the agrochemically active ingredient preferably being a paraquat salt, a diquat salt, a glyphosate or a salt or ester thereof.

4. Sachet according to claim 1 wherein the water-soluble organic polymer(s) is a polyvinyl alcohol polymer.

5. Sachet according to claim 4 wherein the polyvinyl alcohol is 40-100 % alcoholysed or hydrolysed polyvinyl acetate.

6. Sachet according to claim 1 wherein the water-soluble organic polymer(s) is an acrylic polymer bearing carboxyl groups.

7. Sachet according to claim 6 wherein the acrylic polymer(s) comprise a combination of the polymer components S and H, where

S is defined as at least one acid-functional addition copolymer which is soft in character by virtue of having a $T_g \leq 20^\circ\text{C}$, and

H is defined as at least one acid-functional addition copolymer which is hard in character by virtue of having a $T_g \geq 40^\circ\text{C}$,

and wherein further the components S and H are present in a relative weight ratio of S to H within the range of from 90/10 to 65/35 and the acid-functionalities of S and H are at least partly neutralised such as to render the resulting film water-soluble.

8. Sachet according to any one of the preceding claims wherein the film construction of the sachet contains from 1 to 30 wt.%, more preferably 3 to 10 wt.%, based on the total dry weight of the film, of the wax(es).

9. Sachet according to claim 1 wherein the water-dispersible wax(es) has a melting point of $\geq 50^\circ\text{C}$.

10. Sachet according to claim 1 wherein the water-dispersible wax(es) are selected from the list comprising:

petroleum waxes such as paraffin waxes and microcrystalline wax;
animal waxes such as beeswax;
vegetable waxes such as caruba wax and candelilla wax;
mineral waxes such as maston wax and combinations thereof.

11. Sachet according to claim 1 wherein the film construction comprises a laminate construction.
12. Sachet according to claim 11 wherein the laminate construction comprises different polymer films.
13. Sachet according to claim 11 wherein the wax may be incorporated into one or all of the laminate films.
14. Sachet according to any of the preceding claims for packaging a water-based composition in fully or partially sealed form.
15. Combination of a water-soluble sachet and a water-based composition packaged therein, the sachet having a film construction comprising a water-soluble film the binder material of which comprises a water-soluble organic polymer(s), and which film construction incorporates a water-dispersible wax(es) derived from an aqueous dispersion of the wax(es) employed in the formation of the water-soluble film.
16. Combination of a water-soluble sachet and a water-based composition packaged therein, said sachet having having a film construction according to any of the preceding claims.
17. Method of making a sachet according to claim 1 which method comprises preparing a water-soluble film from an aqueous solution or dispersion of a water-soluble organic polymer(s) in admixture with an aqueous dispersion of a wax(es) and forming a sachet whose film construction comprises said water-soluble film.
18. Method of making a sachet according to claim 1 which method comprises preparing a water-soluble film from an aqueous solution or dispersion of a water-soluble polyvinyl alcohol polymer(s) in admixture with an aqueous dispersion of a wax(es) and forming a sachet whose film construction comprises said water-soluble film.
19. Method according to claims 17 and 18 wherein said aqueous dispersion of a wax(es) which is admixed with said aqueous solution or dispersion of a water-soluble organic polymer(s) itself also contains an acrylic polymer in latex or solution form which acrylic polymer is water-soluble or water-insoluble.
20. Method according to claim 19 wherein said acrylic polymer is water-insoluble and has Tg from -20 to 100°C, more preferably from 10 to 50°C.

Patentansprüche

1. Wasserlöslicher Beutel, geeignet zum Verpacken einer Zusammensetzung auf Wasserbasis, wobei der Beutel einen Filmaufbau aufweist, umfassend einen wasserlöslichen Film, dessen Bindemittel (ein) wasserlösliche(s) organische(s) Polymer(e) umfasst und wobei der Filmaufbau (ein) in Wasser dispergierbare(s) Wachs(e) einschließt, welche(s) aus einer wässrigen Dispersion des/r Wachse(s), das/die bei der Bildung des wasserlöslichen Films eingesetzt wird, erhalten wird.
2. Beutel gemäß Anspruch 1, wobei die Zusammensetzung auf Wasserbasis eine auf Wasser basierende Agrochemikalien-, Wäschepflege-, Farbstoff-, Biozid-, industrielle Reinigungszusammensetzung, Mittel zur Oberflächenreinigung im Haushalt oder eine Zusammensetzung im Gesundheitswesen ist.
3. Beutel gemäß Anspruch 2, wobei die Zusammensetzung auf Wasserbasis eine Agrochemikalienzusammensetzung ist, mit einem agrochemischen Wirkstoff der vorzugsweise ein Paraquatsalz, ein Diquatsalz, ein Glyphosat oder ein Salz oder Ester davon ist.
4. Beutel gemäß Anspruch 1, wobei das wasserlösliche organische Polymer ein Polyvinylalkoholpolymer ist.
5. Beutel gemäß Anspruch 4, wobei der Polyvinylalkohol 40 - 100 % alkoholisiertes oder hydrolysiertes Polyvinylacetat ist.

6. Beutel gemäß Anspruch 1, wobei das wasserlösliche organische Polymer ein Carboxylgruppen tragendes Acryl-polymer ist.

7. Beutel gemäß Anspruch 6, wobei das Acrylpolymer eine Kombination der Polymerkomponenten S und H umfasst, wobei

S definiert wird als mindestens ein Additions-copolymer mit Säurefunktionalität das von weicher Beschaffenheit ist, da es eine Tg von ≤ 20 °C besitzt und

H definiert wird als mindestens ein Additions-copolymer mit Säurefunktionalität das von harter Beschaffenheit ist, da es eine Tg von ≥ 40 °C besitzt

und wobei die Komponenten S und H ferner in einem relativen Gewichtsverhältnis von S zu H im Bereich von 90/10 bis 65/35 vorliegen und die Säurefunktionalitäten von S und H zumindest teilweise so neutralisiert sind, dass der resultierende Film wasserlöslich gemacht wird.

8. Beutel gemäß einem der vorhergehenden Ansprüche, wobei der Filmaufbau des Beutels 1 bis 30 Gew.-%, stärker bevorzugt 3 bis 10 Gew.-%, an Wachs(en) enthält, bezogen auf das Gesamtrockengewicht des Films.

9. Beutel gemäß Anspruch 1, wobei das/die in Wasser dispergierbare(n) Wachs(e) einen Schmelzpunkt von ≥ 50 °C aufweist/aufweisen.

10. Beutel gemäß Anspruch 1, wobei das/die in Wasser dispergierbare(n) Wachs(e) ausgewählt wird/werden aus:

petrochemischen Wachsen wie etwa Paraffinwachsen und mikrokristallinen Wachsen,
tierischen Wachsen wie etwa Bienenwachs,
pflanzlichen Wachsen wie etwa Carnaubawachs oder Candelillawachs,
mineralischen Wachsen wie etwa Mastonwachs und Kombinationen davon.

11. Beutel gemäß Anspruch 1, wobei der Filmaufbau einen Laminataufbau umfasst.

12. Beutel gemäß Anspruch 11, wobei der Laminataufbau verschiedene Polymerfilme umfasst.

13. Beutel gemäß Anspruch 11, wobei das Wachs in einen oder allen der Laminatfilme eingebracht werden kann.

14. Beutel gemäß einem der vorhergehenden Ansprüche zum Verpacken einer Zusammensetzung auf Wasserbasis in ganz oder teilweise versiegelter Form.

15. Kombination eines wasserlöslichen Beutels und einer darin verpackten Zusammensetzung auf Wasserbasis, wobei der Beutel einen Filmaufbau aufweist, umfassend einen wasserlöslichen Film, dessen Bindemittel (ein) wasserlösliche(s) organische(s) Polymer(e) umfasst und wobei der Filmaufbau (ein) in Wasser dispergierbare(s) Wachs(e) einschließt, welche(s) aus einer wässrigen Dispersion des/r Wachse(s), das/die bei der Bildung des wasserlöslichen Films eingesetzt wird, erhalten wird.

16. Kombination eines wasserlöslichen Beutels und einer darin verpackten Zusammensetzung auf Wasserbasis, wobei der Beutel einen Filmaufbau gemäß einem der vorhergehenden Ansprüche aufweist.

17. Verfahren zur Herstellung eines Beutels nach Anspruch 1, wobei das Verfahren umfasst:

Herstellen eines wasserlöslichen Films aus einer wässrigen Lösung oder Dispersion von wasserlöslichem/n organischem/n Polymer(en) im Gemisch mit einer wässrigen Dispersion von (einem) Wachs(en) und Bildung eines Beutels, dessen Filmaufbau den wasserlöslichen Film umfasst.

18. Verfahren zur Herstellung eines Beutels nach Anspruch 1, wobei das Verfahren umfasst:

Herstellen eines wasserlöslichen Films aus einer wässrigen Lösung oder Dispersion von wasserlöslichem/n Polyvinylalkoholpolymer(en) im Gemisch mit einer wässrigen Dispersion von (einem) Wachs(en) und Bildung eines Beutels, dessen Filmaufbau den wasserlöslichen Film umfasst.

19. Verfahren gemäß Anspruch 17 und 18, wobei die wässrige Dispersion von (einem) Wachs(en), welche(s) mit der wässrigen Lösung oder Dispersion von wasserlöslichem/n organischem/n Polymer(en) gemischt wird, selbst auch ein Acrylpolymer in Latex- oder gelöster Form enthält, wobei das Acrylpolymer wasserlöslich oder wasserunlöslich ist.

20. Verfahren gemäß Anspruch 19, wobei das Acrylpolymer wasserunlöslich ist und eine Tg von -20 bis 100 °C, stärker bevorzugt von 10 bis 50 °C aufweist.

Revendications

1. Sachet hydrosoluble convenable pour l'emballage d'une composition aqueuse, le sachet ayant une structure de film comprenant un film hydrosoluble dont la matière servant de liant comprend un ou plusieurs polymères organiques hydrosolubles, et structure de film qui renferme une ou plusieurs cires dispersables dans l'eau provenant d'une dispersion aqueuse de la ou des cires utilisées dans la formation du film hydrosoluble.

2. Sachet suivant la revendication 1, dans lequel la composition aqueuse est une composition agrochimique, une composition aqueuse pour la blanchisserie, une matière tinctoriale aqueuse, un biocide aqueux, un produit aqueux de nettoyage industriel, un produit aqueux de nettoyage de surface des habitations ou une composition pour la santé publique.

3. Sachet suivant la revendication 2, dans lequel la composition aqueuse est une composition agrochimique, l'ingrédient agrochimiquement actif étant de préférence un sel de paraquat, un sel de diquat, un glyphosate ou un de ses sels ou esters.

4. Sachet suivant la revendication 1, dans lequel le ou les polymères organiques hydrosolubles consistent en polymère(s) d'alcool polyvinylique.

5. Sachet suivant la revendication 4, dans lequel l'alcool polyvinylique consiste en poly(acétate de vinyle) alcoolisé ou hydrolysé à 40-100 %.

6. Sachet suivant la revendication 1, dans lequel le ou les polymères organiques hydrosolubles consistent en polymère(s) acrylique(s) portant des groupes carboxyle.

7. Sachet suivant la revendication 6, dans lequel le ou les polymères acryliques comprennent une association des constituants polymères S et H, dans laquelle

S désigne au moins un copolymère d'addition à fonctionnalité acide qui est mou en raison d'une $T_g \leq 20^\circ\text{C}$, et

H désigne au moins un copolymère d'addition à fonctionnalité acide qui est dur en raison d'une $T_g \leq 40^\circ\text{C}$,

et dans lequel, en outre, les constituants S et H sont présents en un rapport pondéral relatif de S à H compris dans l'intervalle de 90/10 à 65/35 et les fonctionnalités acides de S et H sont neutralisées au moins partiellement de manière à rendre hydrosoluble le film résultant.

8. Sachet suivant l'une quelconque des revendications précédentes, dans lequel la structure de film du sachet contient 1 à 30 % en poids, plus avantageusement 3 à 10 % en poids, sur la base du poids sec total du film, de la ou des cires.

9. Sachet suivant la revendication 1, dans lequel la ou les cires dispersables dans l'eau ont un point de fusion $\geq 50^\circ\text{C}$.

10. Sachet suivant la revendication 1, dans lequel la ou les cires dispersables dans l'eau sont choisies dans la liste comprenant :

des cires de pétrole telles que des cires paraffiniques et la cire microcristalline ;

des cires animales telles que la cire d'abeille ;

des cires végétales telles que la cire de carnauba et la cire de candelilla ;

des cires minérales telles que la cire maston et leurs associations.

11. Sachet suivant la revendication 1, dans lequel la structure de film comprend une structure stratifiée.
12. Sachet suivant la revendication 11, dans lequel la structure stratifiée comprend des films polymères différents.
- 5 13. Sachet suivant la revendication 11, dans lequel la cire peut être incorporée à l'un des ou la totalité des films stratifiés.
14. Sachet suivant l'une quelconque des revendications précédentes, pour l'emballage d'une composition aqueuse sous forme totalement ou partiellement close hermétiquement.
- 10 15. Association d'un sachet hydrosoluble et d'une composition aqueuse emballée dans ce sachet, le sachet ayant une structure de film comprenant un film hydrosoluble dont la matière servant de liant comprend un ou plusieurs polymères organiques hydrosolubles, et structure de film qui renferme une ou plusieurs cires dispersables dans l'eau provenant d'une dispersion aqueuse de la ou des cires utilisées dans la formation du film hydrosoluble.
- 15 16. Association d'un sachet hydrosoluble et d'une composition aqueuse emballée dans ce sachet, ledit sachet ayant une structure de film suivant l'une quelconque des revendications précédentes.
17. Procédé pour la préparation d'un sachet suivant la revendication 1, qui comprend la préparation d'un film hydro-soluble à partir d'une solution ou dispersion aqueuse d'un ou plusieurs polymères organiques hydrosolubles en mélange avec une dispersion aqueuse d'une ou plusieurs cires et la formation d'un sachet dans la structure de film comprend ledit film hydrosoluble.
- 20 18. Procédé pour la préparation d'un sachet suivant la revendication 1, qui comprend la préparation d'un film hydro-soluble à partir d'une solution ou dispersion aqueuse d'un ou plusieurs polymères d'alcool polyvinylique hydrosolubles en mélange avec une dispersion aqueuse d'une ou plusieurs cires et la formation d'un sachet dans la structure de film comprend ledit film hydrosoluble.
- 25 19. Procédé suivant les revendications 17 et 18, dans lequel la dispersion aqueuse d'une ou plusieurs cires qui est mélangée à la solution ou dispersion aqueuse d'un ou plusieurs polymères organiques hydrosolubles contient elle-même également un polymère acrylique sous forme de latex ou de solution, polymère acrylique qui est hydro-soluble ou insoluble dans l'eau.
- 30 20. Procédé suivant la revendication 19, dans lequel le polymère acrylique est insoluble dans l'eau et a une Tg de -20 à 100°C, plus avantageusement de 10 à 50°C.
- 35