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(54) **PROCESS FOR PREPARING A WATER-SOLUBLE THERMOFORMED CONTAINER**

VERFAHREN ZUR HERSTELLUNG EINES WASSERLÖSLICHEN WARMGEFORMTEN
BEHÄLTERS

PROCEDE DE PREPARATION D'UN RECIPIENT THERMOFORME HYDROSOLUBLE

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WO-A-00/55068 **WO-A-92/17382**
US-A- 4 656 042 **US-A- 5 224 601**

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Description

[0001] The present invention relates to a process for producing a water-soluble article comprising a water-soluble, primary (or "first") thermoformed component and a water-soluble, secondary (or "second") component attached thereto. It also relates to an article obtainable by such a process.

[0002] Thermoforming is a well-known technique for preparing articles from a polymer. It generally comprises heating a polymeric composition, which can be in the form of, for example, a film, to above its softening temperature and thermally deforming the composition in a male or female mould.

[0003] It is also known to package chemical compositions, particularly those which may be of a hazardous or irritant nature, in films. If such compositions are held within water-soluble films forming a container around the compositions, the containers can simply be added to water in order to dissolve or disperse the composition into the water.

[0004] WO 92/17382 discloses a package which corresponds to the preamble of claim 17 containing an agrochemical comprising a first sheet of non-planar water-soluble or water-dispersible material and a second sheet of water-soluble or water-dispersible material superposed on the first sheet and sealed to it.

[0005] A difficulty with this package, however, is that it can only contain a single composition which is compatible with the film. It cannot be used for two compositions which are incompatible with each other or for compositions which are incompatible with the water-soluble or water-dispersible material. For example, WO 92/17382 states that when the package contains the liquid, the liquid must be an organic liquid which contains less than 2 to 3% of water to ensure that it does not attack the film forming the package and cause leakage.

[0006] The present invention provides a process for preparing a water-soluble article comprising a water-soluble primary thermoformed component and a water-soluble secondary component attached to the outside thereof, which comprises placing the secondary component in the cavity of a thermoforming mould, thereafter placing a primary component in or over the thermoforming mould, forming the primary thermoformed component by thermoforming the primary component in the mould, and removing the article from the mould.

[0007] The present invention also provides a water-soluble article comprising a water-soluble primary component which is a thermoformed container containing a primary composition, and a water-soluble secondary component attached to the outside thereof.

[0008] The present invention provides a convenient process for preparing an article comprising a thermoformed primary component, which has a secondary component attached thereto. While it may well be possible to prepare an article by preparing the initial primary component by thermoforming and then attaching the second-

ary component thereto using, for example, an adhesive, the process of the present invention provides a process which can be carried out in a single step, thus eliminating the need to use separate machines.

[0009] Advantageously the present invention also, if desired, allows for the primary component and secondary component to be attached without the need for an adhesive, which may cause problems in some uses.

[0010] The primary component, prior to being placed in or over the thermoforming mould, may be of any shape or form. The primary component may, for example, be in the form of a rigid sheet or a flexible film. The primary component and the secondary component may together form in the finally formed water-soluble article, for example, a strip of a sheet or film (the primary thermoformed component) with one or more compositions such as solid balls or pills (the secondary component) spaced apart along the sheet or film. Individual compositions may then be removed from the sheet or film for individual use. Perforations in the sheet or film may be used to assist separation. The secondary component(s) may be held on the primary component by, for example, mechanical adhesion caused by thermoforming the primary component around the secondary component(s), or by use of an adhesive.

[0011] Desirably, however, in the present invention the primary thermoformed component comprises a polymeric film that has been thermoformed into a desired shape.

[0012] Ideally the primary component is a film which is thermoformed in the mould, thus becoming the primary thermoformed component. Preferably the film of the primary component is formed into a pocket surrounded by a sealing portion. Preferably the process additionally comprises the following process steps thereafter; filling the pocket with a primary composition and closing the pocket, for example by placing a film on top of the filled pocket and across the sealing portion and sealing the films together at the sealing portion.

[0013] Most desirably in the present invention the primary component is a container. The secondary component is then attached to the outside of the container. Such a container can be prepared by thermoforming a film into a pocket surrounded by a sealing portion, filling the pocket with a primary composition and closing the pocket, for example by placing a film on top of the filled pocket and across the sealing portion and sealing the films together at the sealing portion.

[0014] The film may be a single film, or a laminated film as disclosed in GB-A-2,244,258. While a single film may have pinholes, the two or more layers in a laminate are unlikely to have pinholes which coincide. The film is water-soluble (which term is taken to include water-dispersible).

[0015] The term "water-soluble" when used herein means that when used in a washing machine, such as a fabric or dish washing machine, the water-soluble aspects of the article are substantially (greater than 70%, ideally greater than 85%) dissolved or dispersed into the

water. This can be tested by placing the article in 10 litres of agitated water at 45°C for 40 minutes and measuring any undissolved or non-disintegrated pieces of the parts of the article, which are water-soluble, that are left.

[0016] The film may be produced by any process, for example by extrusion and blowing or by casting. The film may be unoriented, monoaxially oriented or biaxially oriented. If the layers in the film are oriented, they usually have the same orientation, although their planes of orientation may be different if desired.

[0017] The layers in a laminate may be the same or different. Thus they may each comprise the same polymer or a different polymer. If it is desired to have a water-soluble laminated film, each of the layers should be water-soluble.

[0018] Examples of water-soluble polymers which may be used in a single layer film or in one or more layers of a laminate are poly(vinyl alcohol) (PVOH) and cellulose derivatives such as hydroxypropyl methyl cellulose (HPMC). An example of a preferred PVOH is ethoxylated PVOH. The PVOH may be partially or fully alcoholised or hydrolysed. For example it may be from 40 to 100%, preferably from 70 to 92%, more preferably about 88% or about 92%, alcoholised or hydrolysed. The degree of hydrolysis is known to influence the temperature at which the PVOH starts to dissolve in water. 88% hydrolysis corresponds to a film soluble in cold (ie room temperature) water, whereas 92% hydrolysis corresponds to a film soluble in warm water.

[0019] The thickness of the film used to produce the pocket is preferably 40 to 300 μm , more preferably 70 to 200 μm , especially 80 to 160 μm , more especially 90 to 150 μm and most especially 90 to 120 μm .

[0020] In a thermoforming process the primary component, preferably a film, may be drawn down or blown down into a mould. Thus, for example, the primary component is heated to the thermoforming temperature using a thermoforming heater plate assembly, and then drawn down under vacuum or blown down under pressure into the mould. In the present invention it is preferred that the film is blown down since the presence of the secondary component in the mould may inhibit the effective use of a vacuum. Plug-assisted thermoforming and pre-stretching the film, for example by blowing the film away from the mould before thermoforming, may, if desired, be used. One skilled in the art can choose an appropriate temperature, pressure or vacuum and dwell time to achieve an appropriate pocket. The amount of vacuum or pressure and the thermoforming temperature used depend on the thickness and porosity of the film and on the polymer or mixture of polymers being used. Thermoforming of PVOH films is known and described in, for example, WO 00/55045.

[0021] A suitable forming temperature for PVOH or ethoxylated PVOH is, for example, from 90 to 130°C, especially 90 to 120°C. A suitable forming pressure is, for example, 69 to 138 kPa (10 to 20 p.s.i.), especially 83 to 117 kPa (12 to 17 p.s.i.). A suitable forming vacuum

is 0 to 4 kPa (0 to 40 mbar), especially 0 to 2 kPa (0 to 20 mbar). A suitable dwell time is, for example, 0.4 to 2.5 seconds, especially 2 to 2.5 seconds.

[0022] While desirably conditions are chosen within the above ranges, it is possible to use one or more of these parameters outside the above ranges, although it may be necessary to compensate by changing the values of the other two parameters.

[0023] Where a pocket is formed from the primary component it may be filled with a desired composition. The pocket may be completely filled or only partially filled. The composition may be a solid. For example, it may be a particulate solid or granulated solid, or a tablet. It may also be a liquid, which may be thickened or gelled if desired. The liquid composition may be non-aqueous or aqueous, for example comprising less than or more than 5% total or free water. The composition may have more than one phase. For example it may comprise an aqueous composition and a liquid composition which is immiscible with the aqueous composition. It may also comprise a liquid composition and a separate solid composition, for example in the form of a ball, pill or speckles.

[0024] After the pocket has been filled it is closed, for example by placing a film on top of the filled pocket and across the sealing portion, and sealing the films together at the sealing portion. This film may be a single-layered film but is desirably laminated to reduce the possibility of pinholes allowing leakage through the film. The film may be the same or different as the film forming the pocket. Examples of suitable films are those given for the film forming the pocket.

[0025] Desirably the covering film has a thickness which is less than that of the film used for forming a pocket because it would not generally be stretched so localised thinning of the sheet will not occur. It is also desirable to have a thickness which is less than that of the film used to form a pocket to ensure a sufficient heat transfer through the film to soften the pocket film if heat sealing is used.

[0026] The thickness of the covering film is generally from 20 to 160 μm , preferably from 40 to 100 μm , such as 40 to 80 μm or 50 to 60 μm .

[0027] The films may be sealed together by any suitable means, for example by means of an adhesive or by heat sealing. Other methods of sealing include infra-red, radio frequency, ultrasonic, laser, solvent, vibration and spin welding. An adhesive such as an aqueous solution of PVOH may also be used. The seal desirably is water-soluble if the containers are water-soluble. The presence of a coating on the sealing portion of the film could hinder or prevent sealing and could cause a reduction in seal strength. Therefore, in the present invention, the sealing portion is preferably left uncoated by the coating composition.

[0028] If heat sealing is used, a suitable sealing temperature is, for example, 120 to 195°C, for example 140 to 150°C. A suitable sealing pressure is, for example, from 250 to 600 kPa. Examples of sealing pressures are

276 to 552 kPa (40 to 80 p.s.i.), especially 345 to 483 kPa (50 to 70 p.s.i.) or 400 to 800 kPa (4 to 8 bar), especially 500 to 700 kPa (5 to 7 bar) depending on the heat sealing machine used. Suitable sealing dwell times are 0.4 to 2.5 seconds.

[0029] One skilled in the art can use an appropriate temperature, pressure and dwell time to achieve a seal of the desired integrity. While desirably conditions are chosen within the above ranges, it is possible to use one or more of these parameters outside the above ranges, although it might be necessary to compensate by changing the values of the other two parameters.

[0030] The secondary component may be any water-soluble components. The term "water-soluble" again includes water-dispersible. Desirably it is not deformed, or is substantially not deformed, during the step wherein the primary component is thermoformed.

[0031] Thus, for example, the secondary component may be in the form of a solid, such as a compressed solid, for example in the form of a ball or pill. It may also itself be a container containing a secondary composition. For example it may comprise a polymeric film containing a secondary composition such as a solid, a gel or a liquid. Such a container may be previously prepared by a thermoforming technique such as that discussed above. It may also be prepared by other means, for example by vertical form fill sealing, injection moulding or blow moulding.

[0032] If the primary composition or secondary composition is incompatible with the films enclosing them, steps have to be taken to improve the compatibility. For example, if the films are water-soluble, the amount of free water in the compositions may be reduced. In particular, an electrolyte or gelling agent may be added. Alternatively a coating may be applied on the inside of the films, for example as disclosed in WO 00/64667 or by coating the inside of the pockets after they have been thermoformed but before they have been filled.

[0033] The primary composition and the composition constituting the secondary component may be the same or different. If they are different they may, nevertheless, have one or more individual components in common. The present invention is especially advantageous when the primary composition and the secondary composition are incompatible with each other since they are separated. It is also advantageous if one of the compositions is incompatible with the components contacting the other composition. For example, the secondary composition may be a composition which is incompatible with the film forming the container containing the primary composition when the secondary composition is itself held within a film. Similarly the primary composition may be a composition which is incompatible with the secondary component or the film containing the secondary composition.

[0034] The secondary component should be chosen such that it does not adversely affect the thermoforming process used to prepare the primary component. In the process of the present invention it is placed in the cavity

of the thermoforming mould as an initial step, for example, by a robot.

[0035] In a thermoforming process air must be evacuated from underneath the primary component as it is being thermoformed. Unless the secondary component is permeable, it will prevent air from being withdrawn from underneath it.

[0036] Therefore the air holes in the thermoforming mould need not be positioned directly underneath the secondary component, although if they are they may help in drawing the primary component down over the secondary component as it is being thermoformed. In particular the mould may, for example, be roughened to assist good air evacuation. Preferably the secondary component should not be placed in a position where a substantial thinning of the primary component can occur if it is in the form of a film. Desirably, therefore, the secondary component is placed at the centre of the bottom of the thermoforming mould, and air is withdrawn from the sides and corners of the mould as well as, optionally, the bottom of the mould around the area on which the secondary component is positioned.

[0037] The mould may contain a recess which is dimensioned so as to accept the secondary component. This is especially advantageous when the secondary component is in the form of a ball since it can simply roll into the recess. The recess may be in any part of the mould, but is desirably near the bottom of the mould, for example on the bottom surface of the mould. It may be at the centre of the bottom surface, or may be off-set to one side. However, the thermoforming mould does not need to contain a recess and the secondary component can simply be placed at the bottom of the mould or on a step positioned above the bottom of the mould.

[0038] During the thermoforming process the primary component, which is usually a polymer, has an elevated temperature. By an appropriate choice of thermoforming temperature and of the secondary component, the primary component will stick to the secondary component at the same time as it is thermoformed. This is especially the case when, for example, the secondary component itself comprises a polymeric film which will be heated to a certain extent by the elevated temperatures within the thermoforming machine or by the contacting of the heated primary component. The mould may also be formed such that the cooling pipes generally used in thermoforming moulds do not cool the area directly under the secondary component.

[0039] Alternatively the secondary component may have an adhesive applied thereto before or after it is placed in the cavity of the thermoforming mould. A suitable adhesive may, for example, be a polymer which is heated in the thermoforming mould, or a component such as water which can act as an adhesive when it contacts the primary component, especially when the primary component is water-soluble. Preferably the primary and secondary components are formed from or are coated with the same water-soluble polymer, this aids adhesion,

especially in the presence of water. The adhesive may, for example, be a heat activated adhesive or coating. The secondary component may also be held on the primary component by mechanical adhesion by ensuring that the primary component flows around and at least partially encloses the secondary component.

[0040] The primary and secondary compositions may independently be any compositions which are intended to be released in an aqueous environment if the container is water-soluble. Thus, for example, either or both compositions may be agrochemical compositions such as a plant protection agent, for instance a pesticide such as an insecticide, fungicide, herbicide, acaricide, or nematocide, a plant growth regulator or a plant nutrient. Such compositions are generally packaged in total amounts of from 0.1 g to 7 kg, preferably 1 to 5 kg, when in solid form. When in liquid or gelled form, such compositions are generally packaged in total amounts of from 1 ml to 10 litres, preferably 0.1 to 6 litres, especially from 0.5 to 1.5 litres.

[0041] The primary and secondary compositions may also independently be fabric care, surface care or dishwashing compositions. Thus, for example, it may be a dishwashing, water-softening, laundry or detergent composition, or a rinse aid. Such compositions may be suitable for use in a domestic washing machine. The primary and secondary compositions may also independently be a disinfectant, antibacterial or antiseptic composition, or a refill composition for a trigger-type spray. Such compositions are generally packaged in total amounts of from 5 to 100 g, especially from 15 to 40 g. For example, a dishwashing composition may weigh from 15 to 30 g, a water-softening composition may weigh from 15 to 40 g.

[0042] The primary composition and the secondary composition may be appropriately chosen depending on the desired use of the article.

[0043] If the article is for use in laundry washing, the primary composition may comprise, for example, a detergent, and the secondary composition may comprise a bleach, stain remover, water-softener, enzyme or fabric conditioner. The article may be adapted to release the compositions at different times during the dish washing cycle. For example, a bleach or fabric conditioner is generally released at the end of a wash, and a water-softener is generally released at the start of a wash. An enzyme may be released at the start or the end of a wash.

[0044] If the article is for use as a fabric conditioner, the primary composition may comprise a fabric conditioner and the secondary component may comprise an enzyme which is released before or after the fabric conditioner in a rinse cycle.

[0045] If the article is for use in dish washing the primary composition may comprise a detergent and the secondary composition may comprise a water-softener, enzyme, rinse aid, bleach or bleach activator. The article may be adapted to release the compositions at different times during the wash. For example, a rinse aid, bleach or bleach activator is preferably released at the end of a

wash, and a water-softener or enzyme is generally released at the start of a wash.

[0046] The primary and secondary compositions, if in liquid form, may independently be anhydrous or comprise water, for example at least 5 wt %, preferably at least 10 wt % free or total water based on the weight of the aqueous compositions. Desirably the compositions contain less than 80 wt % water, ideally less than 50 wt % of water.

[0047] The remaining ingredients of the primary and secondary compositions depend on the use of the compositions. Thus, for example, the compositions may independently contain surface active agents such as an anionic, nonionic, cationic, amphoteric or zwitterionic surface active agents or mixtures thereof.

[0048] Examples of anionic surfactants are straight-chained or branched alkyl sulfates and alkyl polyalkoxylated sulfates, also known as alkyl ether sulfates. Such surfactants may be produced by the sulfation of higher C₈-C₂₀ fatty alcohols.

[0049] Examples of primary alkyl sulfate surfactants are those of formula:



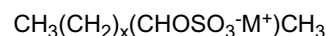
wherein R is a linear C₈-C₂₀ hydrocarbyl group and M is a water-solubilising cation. Preferably R is C₁₀-C₁₆ alkyl, for example C₁₂-C₁₄, and M is alkali metal such as lithium, sodium or potassium.

[0050] Examples of secondary alkyl sulfate surfactants are those which have the sulfate moiety on a "backbone" of the molecule, for example those of formula:



wherein m and n are independently 2 or more, the sum of m+n typically being 6 to 20, for example 9 to 15, and M is a water-solubilising cation such as lithium, sodium or potassium.

[0051] Especially preferred secondary alkyl sulfates are the (2,3) alkyl sulfate surfactants of formulae:



and



for the 2-sulfate and 3-sulfate, respectively. In these formulae x is at least 4, for example 6 to 20, preferably 10 to 16. M is cation, such as an alkali metal, for example lithium, sodium or potassium.

[0052] Examples of alkoxylated alkyl sulfates are ethoxylated alkyl sulfates of the formula:



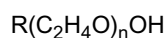
wherein R is a C₈-C₂₀ alkyl group, preferably C₁₀-C₁₈ such as a C₁₂-C₁₆, n is at least 1, for example from 1 to

20, preferably 1 to 15, especially 1 to 6, and M is a salt-forming cation such as lithium, sodium, potassium, ammonium, alkylammonium or alkanolammonium. These compounds can provide especially desirable fabric cleaning performance benefits when used in combination with alkyl sulfates.

[0053] The alkyl sulfates and alkyl ether sulfates will generally be used in the form of mixtures comprising varying alkyl chain lengths and, if present, varying degrees of alkoxylation.

[0054] Other anionic surfactants which may be employed are salts of fatty acids, for example C₈-C₁₈ fatty acids, especially the sodium or potassium salts, and alkyl, for example C₈-C₁₈, benzene sulfonates.

[0055] Examples of nonionic surfactants are fatty acid alkoxyates, such as fatty acid ethoxyates, especially those of formula:



wherein R is a straight or branched C₈-C₁₆ alkyl group, preferably a C₉-C₁₅, for example C₁₀-C₁₄, alkyl group and n is at least 1, for example from 1 to 16, preferably 2 to 12, more preferably 3 to 10.

[0056] The alkoxyated fatty alcohol nonionic surfactant will frequently have a hydrophilic-lipophilic balance (HLB) which ranges from 3 to 17, more preferably from 6 to 15, most preferably from 10 to 15.

[0057] Examples of fatty alcohol ethoxyates are those made from alcohols of 12 to 15 carbon atoms and which contain about 7 moles of ethylene oxide. Such materials are commercially marketed under the trademarks Neodol 25-7 and Neodol 23-6.5 by Shell Chemical Company. Other useful Neodols include Neodol 1-5, an ethoxyated fatty alcohol averaging 11 carbon atoms in its alkyl chain with about 5 moles of ethylene oxide; Neodol 23-9, an ethoxyated primary C₁₂-C₁₃ alcohol having about 9 moles of ethylene oxide; and Neodol 91-10, an ethoxyated C₉-C₁₁ primary alcohol having about 10 moles of ethylene oxide.

[0058] Alcohol ethoxyates of this type have also been marketed by Shell Chemical Company under the Dobanol trademark. Dobanol 91-5 is an ethoxyated C₉-C₁₁ fatty alcohol with an average of 5 moles ethylene oxide and Dobanol 25-7 is an ethoxyated C₁₂-C₁₅ fatty alcohol with an average of 7 moles of ethylene oxide per mole of fatty alcohol.

[0059] Other examples of suitable ethoxyated alcohol nonionic surfactants include Tergitol 15-S-7 and Tergitol 15-S-9, both of which are linear secondary alcohol ethoxyates available from Union Carbide Corporation. Tergitol 15-S-7 is a mixed ethoxyated product of a C₁₁-C₁₅ linear secondary alkanol with 7 moles of ethylene oxide and Tergitol 15-S-9 is the same but with 9 moles of ethylene oxide.

[0060] Other suitable alcohol ethoxyated nonionic surfactants are Neodol 45-11, which is a similar ethylene oxide condensation products of a fatty alcohol having

14-15 carbon atoms and the number of ethylene oxide groups per mole being about 11. Such products are also available from Shell Chemical Company.

[0061] Further nonionic surfactants are, for example, C₁₀-C₁₈ alkyl polyglycosides, such as C₁₂-C₁₆ alkyl polyglycosides, especially the polyglucosides. These are especially useful when high foaming compositions are desired. Further surfactants are polyhydroxy fatty acid amides, such as C₁₀-C₁₈ N-(3-methoxypropyl) glycarnides and ethylene oxide-propylene oxide block polymers of the Pluronic type.

[0062] Examples of cationic surfactants are those of the quaternary ammonium type.

[0063] The total content of surfactants in the composition is desirably 60 to 95 wt%, especially 75 to 90 wt%. Desirably an anionic surfactant is present in an amount of 50 to 75 wt%, the nonionic surfactant is present in an amount of 5 to 50 wt%, and/or the cationic surfactant is present in an amount of from 0 to 20 wt%. The amounts are based on the total solids content of the composition, i.e. excluding any solvent which may be present.

[0064] The primary and secondary compositions, particularly when used as laundry washing or dishwashing compositions, may also independently comprise enzymes, such as protease, lipase, amylase, cellulase and peroxidase enzymes. Such enzymes are commercially available and sold, for example, under the registered trade marks Esperase, Alcalase and Savinase by Nova Industries A/S and Maxatase by International Biosynthetics, Inc. Desirably the enzymes are independently present in the primary or secondary compositions in an amount of from 0.5 to 3 wt%, especially 1 to 2 wt%, when added as commercial preparations they are not pure and this represents an equivalent amount of 0.005 to 0.5 wt% of pure enzyme.

[0065] The primary and secondary compositions may, if desired, independently comprise a thickening agent or gelling agent. Suitable thickeners are polyacrylate polymers such as those sold under the trade mark CARBOPOL, or the trade mark ACUSOL by Rohm and Haas Company. Other suitable thickeners are xanthan gums. The thickener, if present, is generally present in an amount of from 0.2 to 4 wt%, especially 0.5 to 2 wt%.

[0066] Primary or secondary compositions used in dishwashing independently usually comprise a detergent builder. The builders counteract the effects of calcium, or other ion, water hardness. Examples of such materials are citrate, succinate, malonate, carboxymethyl succinate, carboxylate, polycarboxylate and polyacetyl carboxylate salts, for example with alkali metal or alkaline earth metal cations, or the corresponding free acids. Specific examples are sodium, potassium and lithium salts of oxydisuccinic acid, mellitic acid, benzene polycarboxylic acids, C₁₀-C₂₂ fatty acids and citric acid. Other examples are organic phosphonate type sequestering agents such as those sold by Monsanto under the trade mark Dequest and alkylhydroxy phosphonates. Citrate salts and C₁₂-C₁₈ fatty acid soaps are preferred. Further

builders are; phosphates such as sodium, potassium or ammonium salts of mono-, di- or tri-poly or oligo-phosphates; zeolites; silicates, amorphous or structured, such as sodium, potassium or ammonium salts.

[0067] Other suitable builders are polymers and copolymers known to have builder properties. For example, such materials include appropriate polyacrylic acid, polymaleic acid, and polyacrylic/polymaleic and copolymers and their salts, such as those sold by BASF under the trade mark Sokalan.

[0068] The builder is desirably present in an amount of up to 90 wt%, preferably 15 to 90 wt%, more preferably 15 to 75 wt%, relative to the total weight of the composition. Further details of suitable components are given in, for example, EP-A-694,059, EP-A-518,720 and WO 99/06522.

[0069] The primary and secondary compositions can also independently optionally comprise one or more additional ingredients. These include conventional detergent composition components such as further surfactants, bleaches, bleach enhancing agents, builders, suds boosters or suds suppressors, anti-tarnish and anti-corrosion agents, organic solvents, co-solvents, phase stabilisers, emulsifying agents, preservatives, soil suspending agents, soil release agents, germicides, pH adjusting agents or buffers, non-builder alkalinity sources, chelating agents, clays such as smectite clays, enzyme stabilizers, anti-limescale agents, colourants, dyes, hydrotropes, dye transfer inhibiting agents, brighteners, and perfumes. If used, such optional ingredients will generally constitute preferably no more than 15 wt%, for example from 1 to 6 wt%, the total weight of the compositions.

[0070] Primary or secondary compositions which comprise an enzyme may optionally contain materials which maintain the stability of the enzyme. Such enzyme stabilizers include, for example, polyols such as propylene glycol, boric acid and borax. Combinations of these enzyme stabilizers may also be employed. If utilized, the enzyme stabilizers generally constitute from 0.1 to 5 wt%, ideally 0.1 to 1 wt% of the compositions.

[0071] The primary and secondary compositions may independently optionally comprise materials which serve as phase stabilizers and/or co-solvents. Example are C₁-C₃ alcohols such as methanol, ethanol and propanol. C₁-C₃ alkanolamines such as mono-, di- and triethanolamines can also be used, by themselves or in combination with the alcohols. The phase stabilizers and/or co-solvents can, for example, constitute 0 to 1 wt%, preferably 0.1 to 0.5 wt%, of the composition.

[0072] The primary and secondary compositions may independently optionally comprise components which adjust or maintain the pH of the compositions at optimum levels. The pH may be from, for example, 1 to 13, such as 8 to 11 depending on the nature of the composition. For example a dishwashing composition desirably has a pH of 8 to 11, a laundry composition desirable has a pH of 7 to 9, and a water-softening composition desirably

has a pH of 7 to 9. Examples of pH adjusting agents are NaOH and citric acid.

[0073] The above examples may be used for dish or fabric washing. In particular dish washing formulations are preferred which are adapted to be used in automatic dish washing machines. Due to their specific requirements specialised formulation are required and these are illustrated below

[0074] Amounts of the ingredients can vary within wide ranges, however preferred automatic dishwashing detergent compositions herein (which typically have a 1% aqueous solution pH of above 8, more preferably from 9.5 to 12, most preferably from 9.5 to 10.5) are those wherein there is present: from 5% to 90%, preferably from 5% to 75%, of builder; from 0.1% to 40%, preferably from 0.5% to 30%, of bleaching agent; from 0.1% to 15%, preferably from 0.2% to 10%, of the surfactant system; from 0.0001% to 1%, preferably from 0.001% to 0.05%, of a metal-containing bleach catalyst; and from 0.1% to 40%, preferably from 0.1% to 20% of a water-soluble silicate. Such fully-formulated embodiments typically further comprise from 0.1% to 15% of a polymeric dispersant, from 0.01% to 10% of a chelant, and from 0.00001% to 10% of a detergent enzyme, though further additional or adjunct ingredients may be present. Detergent compositions herein in granular form typically limit water content, for example to less than 7% free water, for better storage stability.

[0075] Non-ionic surfactants useful in ADW (Automatic Dish Washing) compositions of the present invention desirably include surfactant (s) at levels of from 2% to 60% of the composition. In general, bleach-stable surfactants are preferred. Non-ionic surfactants generally are well known, being described in more detail in Kirk Othmer's Encyclopedia of Chemical Technology, 3rd Ed., Vol. 22, pp. 360-379, "Surfactants and Detergent Systems", incorporated by reference herein.

[0076] Preferably the ADW composition comprises at least one non-ionic surfactant. One class of non-ionics are ethoxylated non-ionic surfactants prepared by the reaction of a monohydroxy alkanol or alkylphenol with 6 to 20 carbon atoms with preferably at least 12 moles particularly preferred at least 16 moles, and still more preferred at least 20 moles of ethylene oxide per mole of alcohol or alkylphenol.

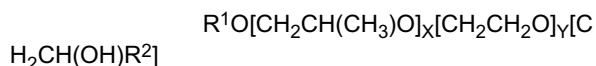
[0077] Particularly preferred non-ionic surfactants are the non-ionic from a linear chain fatty alcohol with 16-20 carbon atoms and at least 12 moles particularly preferred at least 16 and still more preferred at least 20 moles of ethylene oxide per mole of alcohol.

[0078] According to one preferred embodiment the non-ionic surfactant additionally comprise propylene oxide units in the molecule. Preferably this PO units constitute up to 25% by weight, preferably up to 20% by weight and still more preferably up to 15% by weight of the overall molecular weight of the non-ionic surfactant. Particularly preferred surfactants are ethoxylated monohydroxy alkanols or alkylphenols, which additionally

comprises polyoxyethylene-polyoxypropylene block copolymer units. The alcohol or alkylphenol portion of such surfactants constitutes more than 30%, preferably more than 50%, more preferably more than 70% by weight of the overall molecular weight of the non-ionic surfactant.

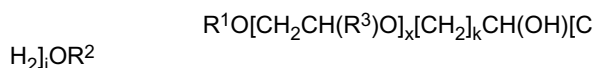
[0079] Another class of non-ionic surfactants includes reverse block copolymers of polyoxyethylene and polyoxypropylene and block copolymers of polyoxyethylene and polyoxypropylene initiated with trimethylolpropane.

[0080] Another preferred non-ionic surfactant can be described by the formula:



wherein R^1 represents a linear or branched chain aliphatic hydrocarbon group with 4-18 carbon atoms or mixtures thereof, R^2 represents a linear or branched chain aliphatic hydrocarbon rest with 2-26 carbon atoms or mixtures thereof, x is a value between 0.5 and 1.5 and y is a value of at least 15.

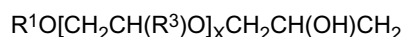
[0081] Another group of preferred nonionic surfactants are the end-capped polyoxyalkylated non-ionics of formula:



wherein R^1 and R^2 represent linear or branched chain, saturated or unsaturated, aliphatic or aromatic hydrocarbon groups with 1-30 carbon atoms, R^3 represents a hydrogen atom or a methyl, ethyl, n-propyl, iso-propyl, n-butyl, 2-butyl or 2-methyl-2-butyl group, x is a value between 1 and 30 and, k and j are values between 1 and 12, preferably between 1 and 5. When the value of x is ≥ 2 each R^3 in the formula above can be different. R^1 and R^2 are preferably linear or branched chain, saturated or unsaturated, aliphatic or aromatic hydrocarbon groups with 6-22 carbon atoms, where group with 8 to 18 carbon atoms are particularly preferred. For the group R^3 H, methyl or ethyl are particularly preferred. Particularly preferred values for x are comprised between 1 and 20, preferably between 6 and 15.

[0082] As described above, in case $x \geq 2$, each R^3 in the formula can be different. For instance, when $x=3$, the group R^3 could be chosen to build ethylene oxide ($R^3=H$) or propylene oxide ($R^3=methyl$) units which can be used in every single order for instance (PO) (EO) (EO), (EO) (PO) (EO), (EO) (EO) (PO), (EO) (EO) (EO), (PO) (EO) (PO), (PO) (PO) (EO) and (PO) (PO) (PO). The value 3 for x is only an example and bigger values can be chosen whereby a higher number of variations of (EO) or (PO) units would arise.

[0083] Particularly preferred end-capped polyoxyalkylated alcohols of the above formula are those where $k=1$ and $j=1$ originating molecules of simplified formula:



OR²

[0084] The use of mixtures of different non-ionic surfactants is particularly preferred in ADW formulations for example mixtures of alkoxyated alcohols and hydroxy group containing alkoxyated alcohols.

[0085] In the present invention, if more than one article, for example a container, is formed at the same time from the same sheet, the articles may then be separated from each other by cutting the portions between them, for example the sealing portions or flanges. Alternatively, they may be left conjoined and, for example, perforations provided between the individual articles so that they can be easily separated at a later stage, for example by a consumer. If the articles are separated, the flanges may be left in place. However, desirably the flanges are partially removed in order to provide an even more attractive appearance. Generally the flanges remaining should be as small as possible for aesthetic purposes while bearing in mind that some flange is required if the articles are in the form of thermoformed containers to ensure the two films remain adhered to each other. A flange having a width of 1 mm to 8 mm is desirable, preferably 2 mm to 7 mm, most preferably about 5 mm.

[0086] The articles, for example containers, may be packaged in outer containers if desired, for example non-water soluble containers which are removed before the water-soluble articles are used.

[0087] The containers produced by the process of the present invention, especially when used for a fabric care, surface care or dishwashing composition, may have a maximum dimension of 5 cm, excluding any flanges. For example, a container may have a length of 1 to 5 cm, especially 3.5 to 4.5 cm, a width of 1.5 to 3.5 cm, especially 2 to 3 cm, and a height of 1 to 2 cm, especially 1.25 to 1.75 cm.

Claims

1. A process for preparing a water-soluble article comprising a water-soluble primary thermoformed component and a water-soluble secondary component attached to the outside thereof, which comprises placing the secondary component in the cavity of a thermoforming mould, thereafter placing a primary component in or over the thermoforming mould, forming the primary thermoformed component by thermoforming the primary component in the mould, and removing the article from the mould.
2. A process according to claim 1 wherein the primary component is a film.
3. A process according to claim 1 wherein the primary thermoformed component comprises a film.
4. A process according to any claim from 1 to 3 wherein

the primary component is thermoformed into a pocket surrounded by a sealing portion and wherein the process additionally comprises the steps of filling the pocket with a primary composition and closing the pocket, for example by placing a film on top of the filled pocket and across the sealing portion and sealing the polymeric films together at the sealing portion.

5. A process according to claim 1 or 3 wherein the primary component is a sealed container containing a primary composition. 10
6. A process according to claim 5 wherein the sealed container is prepared by thermoforming a film into a pocket surrounded by a sealing portion, filling the pocket with a primary composition and closing the pocket, for example by placing a film on top of the filled pocket and across the sealing portion and sealing the films together at the sealing portion. 20
7. A process according to any claim from 4 to 6 wherein the composition is a solid, a gel or a liquid.
8. A process according to any one of the preceding claims wherein the secondary component is a compressed solid or a container containing a secondary composition. 25
9. A process according to claim 8 wherein the secondary component is a container comprising a polymeric film containing a solid, a gel or a liquid. 30
10. A process according to any one of the preceding claims wherein the primary component and/or the secondary component comprises a poly(vinyl alcohol). 35
11. A process according to any one of the preceding claims wherein the article is for use in dishwashing, fabric care or surface care. 40
12. A process according to claim 11 wherein the primary component comprises a dishwashing, water-softening, laundry or detergent composition. 45
13. A process according to claim 11 or 12 wherein the secondary component comprises a dishwashing, water-softening, laundry or detergent composition or a rinse-aid. 50
14. A process according to any one of claims 1 to 10 wherein the primary component and/or secondary component comprises a disinfectant, antibacterial or antiseptic composition. 55
15. A process according to any one of claims 1 to 10 or 14 wherein the article comprises a refill composition

for a trigger-type spray.

16. A process according to any one of claims 1 to 10 wherein the article comprises an agricultural composition. 5
17. A water-soluble article comprising a water-soluble primary component which is a thermoformed container containing a primary composition, **characterized in that** a water-soluble secondary component is attached to the outside of the thermoformed container. 10
18. An article according to claim 17 wherein the primary composition is a solid, a gel or a liquid. 15
19. An article according to claim 17 or 18 wherein the secondary component is a compressed solid or a container containing a secondary composition. 20
20. An article according to claim 19 wherein the secondary component is a container comprising a polymeric film containing a solid, a gel or a liquid.
21. An article according to any one of claims 17 to 20 wherein the primary component and/or the secondary component comprises a poly(vinyl alcohol). 25
22. An article according to any one of claims 17 to 21 wherein the article is for use in dishwashing, fabric care or surface care. 30
23. An article according to claim 22 wherein the primary composition is a dishwashing, water-softening, laundry or detergent composition. 35
24. An article according to claim 22 or 23 wherein the secondary component comprises a dishwashing, water-softening, laundry or detergent composition or a rinse-aid. 40
25. An article according to any one of claims 18 to 21 wherein the primary composition and/or secondary component comprises a disinfectant, antibacterial or antiseptic composition. 45
26. An article according to any one of claims 18 to 21 or 25 wherein the article comprises a refill composition for a trigger-type spray. 50
27. An article according to any one of claims 17 to 21 wherein the article comprises an agricultural composition. 55

Revendications

1. Procédé de fabrication d'un article hydrosoluble

- comprenant un composant primaire thermoformé hydrosoluble et un composant secondaire hydrosoluble attaché à l'extérieur de celui-ci, qui comprend les étapes consistant à placer le composant secondaire dans la cavité d'un moule de thermoformage, puis à placer un composant primaire dans ou sur le moule de thermoformage, à former le composant primaire thermoformé par thermoformage du composant primaire dans le moule, et à retirer l'article du moule.
2. Procédé selon la revendication 1, dans lequel le composant primaire est un film.
 3. Procédé selon la revendication 1, dans lequel le composant primaire thermoformé comprend un film.
 4. Procédé selon l'une quelconque des revendications 1 à 3, dans lequel le composant primaire est thermoformé en une poche entourée d'une zone de scellage et dans lequel le procédé comprend de plus les étapes consistant à remplir la poche avec une composition primaire et à fermer la poche, par exemple en plaçant un film sur le dessus de la poche remplie et en travers de la zone de scellage et à sceller les films polymères ensemble au niveau de la zone de scellage.
 5. Procédé selon la revendication 1 ou 3, dans lequel le composant primaire est un récipient scellé contenant une composition primaire.
 6. Procédé selon la revendication 5, dans lequel le récipient scellé est fabriqué en thermoformant un film en une poche entourée d'une zone de scellage, en remplissant la poche avec une composition primaire et en fermant la poche, par exemple en plaçant un film sur le dessus de la poche remplie et en travers la zone de scellage et en scellant les films ensemble au niveau de la zone de scellage.
 7. Procédé selon l'une quelconque des revendications 4 à 6, dans lequel la composition est un solide, un gel ou un liquide.
 8. Procédé selon l'une quelconque des revendications précédentes, dans lequel le composant secondaire est un solide comprimé ou un récipient contenant une composition secondaire.
 9. Procédé selon la revendication 8, dans lequel le composant secondaire est un récipient comprenant un film polymère contenant un solide, un gel ou un liquide.
 10. Procédé selon l'une quelconque des revendications précédentes, dans lequel le composant primaire et/ou le composant secondaire comprennent un poly(alcool vinylique).
 11. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'article est destiné à être utilisé dans le lavage de la vaisselle, l'entretien de tissus ou l'entretien de surfaces.
 12. Procédé selon la revendication 11, dans lequel le composant primaire comprend une composition pour le lavage de la vaisselle, l'adoucissement de l'eau, le lavage du linge ou détergente.
 13. Procédé selon la revendication 11 ou 12, dans lequel le composant secondaire comprend une composition pour lavage de la vaisselle, l'adoucissement de l'eau, le lavage du linge ou détergente ou un adjuvant de rinçage.
 14. Procédé selon l'une quelconque des revendications 1 à 10, dans lequel le composant primaire et/ou le composant secondaire comprennent une composition désinfectante, antibactérienne ou antiseptique.
 15. Procédé selon l'une quelconque des revendications 1 à 10 ou 14 dans lequel l'article comprend une composition de recharge pour un pulvérisateur du type à gâchette.
 16. Procédé selon l'une quelconque des revendications 1 à 10, dans lequel l'article comprend une composition à usage agricole.
 17. Article hydrosoluble comprenant un composant primaire hydrosoluble qui est un récipient thermoformé contenant une composition primaire, **caractérisé en ce qu'un** composant secondaire hydrosoluble est attaché à l'extérieur du récipient thermoformé.
 18. Article selon la revendication 17, dans lequel la composition primaire est un solide, un gel ou un liquide.
 19. Article selon la revendication 17 ou 18, dans lequel le composant secondaire est un solide comprimé ou un récipient contenant une composition secondaire.
 20. Article selon la revendication 19, dans lequel le composant secondaire est un récipient comprenant un film polymère contenant un solide, un gel ou un liquide.
 21. Article selon l'une quelconque des revendications 17 à 20, dans lequel le composant primaire et/ou le composant secondaire comprennent un poly(alcool vinylique).
 22. Article selon l'une quelconque des revendications 17 à 21, dans lequel l'article est destiné à être utilisé dans le lavage de la vaisselle, l'entretien de tissus

ou l'entretien de surfaces.

23. Article selon la revendication 22, dans lequel la composition primaire est une composition pour le lavage de la vaisselle, l'adoucissement de l'eau, le lavage du linge ou détergente. 5
24. Article selon la revendication 22 ou 23, dans lequel le composant secondaire comprend une composition pour le lavage de la vaisselle, l'adoucissement de l'eau, le lavage du linge ou détergente ou un adjuvant de rinçage. 10
25. Article selon l'une quelconque des revendications 18 à 21, dans lequel la composition primaire et/ou le composant secondaire comprennent une composition désinfectante, antibactérienne ou antiseptique. 15
26. Article selon l'une quelconque des revendications 18 à 21 ou 25, dans lequel l'article comprend une composition de recharge pour un pulvérisateur du type à gâchette. 20
27. Article selon l'une quelconque des revendications 17 à 21, dans lequel l'article comprend une composition à usage agricole. 25

Patentansprüche

1. Verfahren zur Herstellung eines wasserlöslichen Gegenstands, umfassend einen wasserlöslichen ersten warmgeformten Bestandteil und einen an der Außenseite davon angebrachten wasserlöslichen zweiten Bestandteil, welches das Positionieren des zweiten Bestandteils in den Hohlraum einer Warmformungsform umfasst, wonach ein erster Bestandteil in oder auf die Warmformungsform positioniert wird, der erste warmgeformte Bestandteil durch Warmformen des ersten Bestandteils in der Form geformt wird und der Gegenstand aus der Form entfernt wird. 30
2. Verfahren nach Anspruch 1, wobei der erste Bestandteil eine Folie ist. 35
3. Verfahren nach Anspruch 1, wobei der erste warmgeformte Bestandteil eine Folie umfasst. 40
4. Verfahren nach einem der Ansprüche 1 bis 3, wobei der erste Bestandteil zu einem von einem Versiegelungsteil umgebenen Beutel warmgeformt wird und das Verfahren zusätzlich die Schritte des Füllens des Beutels mit einer ersten Zusammensetzung und Verschließen des Beutels z.B. durch Positionieren einer Folie auf dem gefüllten Beutel und über dem Versiegelungsteil und Versiegeln der Polymerfolien umfasst. 45

miteinander umfasst.

5. Verfahren nach Anspruch 1 oder 3, wobei der erste Bestandteil ein versiegelter Behälter ist, der eine erste Zusammensetzung umfasst. 50
6. Verfahren nach Anspruch 5, wobei der versiegelte Behälter durch Warmformen einer Folie zu einem von einem Versiegelungsteil umgebenen Beutel, Füllen des Beutels mit einer ersten Zusammensetzung und Verschließen des Beutels z.B. durch Positionieren einer Folie auf dem gefüllten Beutel und über dem Versiegelungsteil und Versiegeln der Folien miteinander am Versiegelungsteil umfasst. 55
7. Verfahren nach einem der Ansprüche 4 bis 6, wobei die Zusammensetzung ein Feststoff, ein Gel oder eine Flüssigkeit ist.
8. Verfahren nach einem der vorangehenden Ansprüche, wobei der zweite Bestandteil ein komprimierter Feststoff oder eine zweite Zusammensetzung enthaltender Behälter ist.
9. Verfahren nach Anspruch 8, wobei der zweite Bestandteil ein Behälter ist, der einen Feststoff, ein Gel oder eine Flüssigkeit enthaltende Polymerfolie umfasst.
10. Verfahren nach einem der vorangehenden Ansprüche, wobei der erste Bestandteil und/oder der zweite Bestandteil einen Poly(vinylalkohol) umfassen.
11. Verfahren nach einem der vorangehenden Ansprüche, wobei der Gegenstand beim Geschirrspülen, bei der Gewebepflege oder Oberflächenpflege verwendet wird.
12. Verfahren nach Anspruch 11, wobei der erste Bestandteil eine Geschirrspül-, Wasserenthärter-, Wäschewasch- oder Detergensenzymzusammensetzung umfasst.
13. Verfahren nach Anspruch 11 oder 12, wobei der zweite Bestandteil eine Geschirrspül-, Wasserenthärter-, Wäschewasch- oder Detergensenzymzusammensetzung oder eine Spülhilfe umfasst.
14. Verfahren nach einem der Ansprüche 1 bis 10, wobei der erste Bestandteil und/oder der zweite Bestandteil eine desinfizierende, antibakterielle oder antiseptische Zusammensetzung umfassen.
15. Verfahren nach einem der Ansprüche 1 bis 10 oder 14, wobei der Gegenstand eine Nachfüllzusammensetzung für ein Pumpspray umfasst.
16. Verfahren nach einem der Ansprüche 1 bis 10, wobei

der Gegenstand eine landwirtschaftliche Zusammensetzung umfasst.

17. Wasserlöslicher Gegenstand, umfassend einen wasserlöslichen ersten Bestandteil, bei welchem es sich um einen warmgeformten Behälter handelt, der eine erste Zusammensetzung enthält, **dadurch gekennzeichnet, dass** ein wasserlöslicher zweiter Bestandteil an der Außenseite des warmgeformten Behälters angebracht ist. 5
10
18. Gegenstand nach Anspruch 17, wobei die erste Zusammensetzung ein Feststoff, ein Gel oder eine Flüssigkeit ist. 15
19. Gegenstand nach Anspruch 17 oder 18, wobei der zweite Bestandteil ein komprimierter Feststoff oder ein eine zweite Zusammensetzung enthaltender Behälter ist. 20
20. Gegenstand nach Anspruch 19, wobei der zweite Bestandteil ein Behälter ist, der eine einen Feststoff, ein Gel oder eine Flüssigkeit enthaltende Polymerfolie umfasst. 25
21. Gegenstand nach einem der Ansprüche 17 bis 20, wobei der erste Bestandteil und/oder der zweite Bestandteil einen Poly(vinylalkohol) umfassen.
22. Gegenstand nach einem der Ansprüche 17 bis 21, wobei der Gegenstand beim Geschirrspülen, bei der Gewebepflege oder Oberflächenpflege verwendet wird. 30
23. Gegenstand nach Anspruch 22, wobei der erste Bestandteil eine Geschirrspül-, Wasserenthärter-, Wäschewasch- oder Detergensenzymzusammensetzung umfasst. 35
24. Gegenstand nach Anspruch 22 oder 23, wobei der zweite Bestandteil eine Geschirrspül-, Wasserenthärter-, Wäschewasch- oder Detergensenzymzusammensetzung oder eine Spülhilfe umfasst. 40
25. Gegenstand nach einem der Ansprüche 18 bis 21, wobei die erste Zusammensetzung und/oder der zweite Bestandteil eine desinfizierende, antibakterielle oder antiseptische Zusammensetzung umfasst. 45
50
26. Gegenstand nach einem der Ansprüche 18 bis 10 oder 21, wobei der Gegenstand eine Nachfüllzusammensetzung für ein Pumpspray umfasst.
27. Gegenstand nach einem der Ansprüche 17 bis 21, wobei der Gegenstand eine landwirtschaftliche Zusammensetzung umfasst. 55