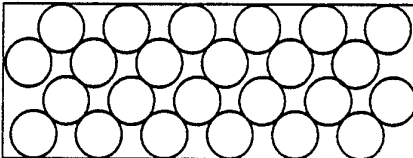




## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification <sup>5</sup> : <b>B65D 65/46, A01N 25/34</b></p>	<p><b>A1</b></p>	<p>(11) International Publication Number: <b>WO 94/02377</b> (43) International Publication Date: 3 February 1994 (03.02.94)</p>
<p>(21) International Application Number: PCT/US93/06565 (22) International Filing Date: 16 July 1993 (16.07.93) (30) Priority data: 07/916,807 20 July 1992 (20.07.92) US (60) Parent Application or Grant (63) Related by Continuation US 07/916,807 (CIP) Filed on 20 July 1992 (20.07.92) (71) Applicant (for all designated States except US): E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).</p>	<p>(72) Inventor; and (75) Inventor/Applicant (for US only): BERGER, Richard, Alan [US/US]; 3 Dustin Drive, Claymont, DE 19703-1107 (US). (74) Agents: MAYER, Nancy, S. et al.; E.I. du Pont de Nemours and Company, Legal/Patents Records Center, 1007 Market Street, Wilmington, DE 19898 (US). (81) Designated States: AU, BB, BG, BR, BY, CA, CZ, FI, HU, JP, KP, KR, KZ, LK, MG, MN, MW, NO, NZ, PL, RO, RU, SD, SK, UA, US, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p><b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>	
<p>(54) Title: CELLULAR-AIR WATER-SOLUBLE FILM PACKAGING</p>		
<div style="text-align: center;">  </div>		
<p>(57) Abstract</p> <p>Cellular-air water-soluble film which can be used for packaging is disclosed as well as various package forms, some of which are buoyant in a water medium and some of which provide sub-unit chemical dosage forms.</p>		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	MR	Mauritania
AU	Australia	GA	Gabon	MW	Malawi
BB	Barbados	GB	United Kingdom	NE	Niger
BE	Belgium	GN	Guinea	NL	Netherlands
BF	Burkina Faso	GR	Greece	NO	Norway
BG	Bulgaria	HU	Hungary	NZ	New Zealand
BJ	Benin	IE	Ireland	PL	Poland
BR	Brazil	IT	Italy	PT	Portugal
BY	Belarus	JP	Japan	RO	Romania
CA	Canada	KP	Democratic People's Republic of Korea	RU	Russian Federation
CF	Central African Republic	KR	Republic of Korea	SD	Sudan
CG	Congo	KZ	Kazakhstan	SE	Sweden
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovak Republic
CM	Cameroon	LU	Luxembourg	SN	Senegal
CN	China	LV	Latvia	TD	Chad
CS	Czechoslovakia	MC	Monaco	TG	Togo
CZ	Czech Republic	MG	Madagascar	UA	Ukraine
DE	Germany	ML	Mali	US	United States of America
DK	Denmark	MN	Mongolia	UZ	Uzbekistan
ES	Spain			VN	Viet Nam
FI	Finland				

TITLE

## CELLULAR-AIR WATER-SOLUBLE FILM PACKAGING

The present invention relates to the field of  
5 cellular-air water-soluble film which can be used in  
bag and sheet form to package delicate or fragile  
items. Such film is particularly advantageous in  
packaging and delivering an agricultural chemical to a  
water medium.

10 Packaging constitutes a large volume of material  
for waste disposal. The long decomposition time for  
many types of materials used in packaging creates  
environmental problems of a significant magnitude.  
There is a need for packaging which is easily  
15 disposable and results in less of an adverse impact on  
the environment. In response, packaging prepared from  
water-soluble films or sheets has been developed.  
However, such materials provide little cushioning or  
insulation to the items enclosed therein. A need  
20 exists for improved water-soluble packaging.

In the area of agricultural chemicals, EP 347,219;  
347,220; 347,221; and 347,222 (May and Baker) each  
disclose a water-soluble or water dispersible envelope  
containing liquid pesticide(s). The envelope is  
25 preferably only partly full so that air space occupies  
2% to 40% of the volume. Partial filling of the  
envelope is stated to reduce the risk of rupture by  
shock or temperature increase.

Difficulties exist with present commercial water-  
30 soluble bags for agricultural chemicals. When a  
package is added to a mix tank of water there is the  
tendency for the bag to sink immediately, and then  
migrate towards and eventually rest on the suction  
intake of an agricultural sprayer circulation system.  
35 Mix tank circulation patterns and the suction from the  
tank pump direct the bags towards the suction intake.

The bag can easily conform to the shape of the intake, block circulation and starve the pump. Another problem with a commercial water-soluble bag which sinks immediately is the potential for the bag to become

5 lodged against part of the internal piping at the tank bottom, or rest at the bottom in a zone experiencing poor circulation. Water-soluble bags in these situations can leave undispersed product (e.g., as oily blotches) at the bottom of the tank. Another

10 disadvantage is that such bags are only available in single dose units. Only whole water-soluble packages are used when tank mixing, and therefore the package size limits the dose of product. Suppliers typically stock large inventories of package sizes to be flexible

15 in meeting the needs of their customers. Also conventional water-soluble packages are designed to deliver only one chemical product. In practice, mixing of two or more agricultural chemicals which can be mutually incompatible as concentrates, is often

20 desirable. Product leakage during shipment or handling with conventional bags, especially in cold weather, can result from cracks in the heat seal or film from impacts and can expose workers to potentially hazardous chemicals.

25 Thus, a need exists for improved water-soluble packaging in general and for agricultural chemicals in particular for safety as well as environmental reasons. The cellular-air water-soluble film packages of the present invention overcome many of the problems

30 discussed above with packages known in the art, and in addition, provide added advantages over them.

#### SUMMARY OF THE INVENTION

The present invention comprises cellular-air water-soluble film comprising a water soluble polymer sheet

35 having one or more discrete air cells on its surface. The film may further comprise a plasticizer. The

present invention further comprises containers or packages fabricated from such a film. The containers may be of various sizes and geometric shapes. Included within the present invention are bags, filled-cell  
5 packages, filled laminate packages, and filled film, and combinations thereof.

The present invention further comprises a package for delivering chemicals, in particular agricultural chemicals, comprising (1) a film of a water-soluble  
10 polymeric sheet having one or more discrete air cells on its surface containing air equal to from about 5% to about 50% by volume of a delivered chemical, and (2) at least one chemical. One or more chemicals can be contained within at least one of the air cells.  
15 Alternatively, or in addition, at least one chemical can be dispersed within the polymer sheet forming the film. An additional package of this type can have at least one chemical contained within a container fabricated from the film. Air can be contained within  
20 the container as well as in the air cells, and comprise part of the 5% to 50% by volume of the delivered chemical thereby providing buoyancy.

The present invention further comprises a package for delivering chemicals, in particular agricultural  
25 chemicals, comprising one or more laminates of (1) a first film of a water-soluble polymeric sheet having one or more discrete air cells on its surface, (2) a second film of a water-soluble polymeric sheet of the same or different composition and thickness, laminated  
30 to the first film on one or both sides from which the air cells protrude, and (3) at least one chemical, such that said laminate has a total amount of air in the cells or in a package formed from said laminate equal to from about 5% to about 50% by volume of the  
35 delivered chemical. The chemical(s) can be contained in the spaces between the first and second films around

the air cells. Alternatively, or in addition, the package can have at least one chemical independently dispersed within the polymeric sheet forming the film. Alternatively, or in addition, one or more chemicals  
5 can be contained in at least one of the air cells. Such laminates can be fabricated into containers, such as bags, which contain air and an additional distinct chemical. The air in the container can comprise part of the 5% to 50% by volume of the delivered chemical  
10 providing buoyancy.

The above described packages can be perforated between at least two discrete groups of air cells to allow for convenient sub-unit dosing. For greatest flexibility in sub-unit dosing, the package is  
15 perforated between each air cell.

#### BRIEF DESCRIPTION OF THE FIGURES

Figure 1 is a plan view of one form of the film of the present invention.

20 Figure 2 is a plan view of one form of the film of the present invention which possesses discrete space with no air cells on its surface.

Figure 3 is a plan view of a package of the present invention having individual dose capacity of different compositions via perforations.

25 Figure 4 is a cross sectional view of a laminated package of the present invention having chemicals and air contained in discrete cells bonded on each side with a film containing chemical dispersed therein. "A" indicates spaces between cells that may also contain  
30 air within the laminated structure.

#### DETAILED DESCRIPTION OF THE INVENTION

The present invention comprises a film comprising a water-soluble polymer sheet having one or more discrete air cells on its surface. The cellular-air film can be  
35 formed from any flat film which is soluble in water and has good thermoplastic or thermoforming properties.

Suitable cold-water-soluble polymers can comprise polyvinyl alcohol, vinyl alcohol copolymers (e.g., vinyl alcohol/vinyl esters such as vinyl alcohol/vinyl acetates), vinyl pyrrolidone/vinyl acetate, 5 polyethylene oxide, water-soluble cellulose derivatives (e.g., methyl cellulose, hydroxyethyl cellulose, hydroxypropyl methyl cellulose, etc.), starchs, gelatin, polyvinyl pyrrolidone, or copolymers such as poly(vinyl pyrrolidone/vinyl acetate), copolyesters 10 made from hydroxyvaleric acid and hydroxybutyric acid, copolymers of ethylene and acrylic acid, or copolymers of ethylene and methyl acrylic acid. The preferred polymer film is composed of polyvinyl alcohol. The films can further comprise a plasticizer such that the 15 composition has suitable thermoplastic properties. Preferred plasticizers are polyethylene glycol or glycerol. Films may be cast, blown or extruded. Films may be clear or prepared in a particular desired color or pattern. The desired film characteristics such as 20 thickness, thermoplasticity, fusion temperature, film elongation, disintegration-dissolution time, tensile strength, tear resistance, color, etc. depend on the polymers employed and specific utility and can be determined by one skilled in the art.

25 The film may be comprised of a plurality of individual polymer sheets fused together having the same or different thickness and composition. Such multilayer sheets help to avoid any pinholes in the finished cellular-air film, which would be of 30 particular concern when packaging liquids. The term "sheet" or "sheets" as used herein includes both a single sheet of a water-soluble polymer or a sheet comprised of a plurality of individual polymer sheets fused together. The film thickness used is that which 35 is sufficiently tough and flexible to withstand fabrication, incorporation of air capsules, filling

with the chemical(s), and handling. Individual film thicknesses are typically from about 20 to 500 microns, preferably 20-100 microns.

Air is incorporated in one or more sealed self-contained capsules or cells on the surface of the water-soluble film. The shape, positioning, size distribution and total volume of the air cells on the film surface are highly variable. The size, shape, and configuration of the individual cells can vary depending upon the desired use. The cells can be uniform in size or vary in size. Typically the cells have a diameter of from about 0.5 cm to about 25 cm. Examples are shown in Figures 1 and 2. Examples of suitable air cell shapes include bubbles (ovular or circular aligned in rows or in "checkerboard" fashion, bar-shaped in a ribbed configuration), or a doughnut (with an air-free film zone in the center targeted for quick dissolution and release of the contents, see Figure 2). The dissolution time is dependent upon the polymer employed in the film. Depending on the polymer the packages dissolve in both warm and cold water, preferably at temperatures as low as 5 to 10°C. The films and packages of the present invention can be made so that they begin to visibly disintegrate in less than one minute in an aqueous medium, preferably less than 30 seconds, and will totally dissolve in less than 10 minutes, preferably less than 2 minutes.

The water-soluble cellular-air film itself can be used for packaging and shipping generally or to manufacture a variety of containers or package types. The present invention comprises packages or containers such as bags, filled-cell packages, filled film, filled laminate packages and combinations thereof. The film and packages of the present invention are particularly suitable for delivery of chemicals to a water medium. The term "chemical" or "chemical product" or "delivered



chemical" is used herein to mean a single chemical, a mixture of chemicals, or a composition in solid, liquid, or gel form and includes agricultural chemicals, water treatment chemicals, pharmaceutical chemicals, detergent chemicals, household chemicals, research chemicals, and other chemical products. Intended are chemicals for delivery to, application to, or use at a specific locus which are distinct from and in addition to the film components.

10 (1) One package type of the present invention is a bag, in which a chemical is sealed inside a container fabricated from the water soluble cellular-air film of the present invention. The term "bag" is defined herein to be a conventional rectangular pouch or a  
15 variety of other geometrical shapes including a tube, ball, doughnut, envelope, cube or other polygon. The air capsules can project out from the exterior or into the interior of the bag. In addition, the cells can be distributed uniformly throughout the bag or cover one  
20 portion, e.g., only on one side, only along the edges, etc. A strategic area on the surface of a bag may be intentionally left void of air cells to serve as a quick dissolution release zone. The bags are sealed (e.g., heat sealed) around the edges creating an open  
25 cavity to be filled with a chemical product. Sealing may also be accomplished under pressure using a solvent seal (i.e., water or aqueous solution of resin) or by use of ultrasound or other known techniques.

(2) A second package type of the present  
30 invention is a filled-cell package, used herein to denote cellular-air water soluble film, in which one or more air cells are partially filled with at least one chemical product. The buoyancy of the package results from the air void space in each of the partially filled  
35 cells. Alternatively, some cells could be completely filled with chemical, and some contain only air to

provide buoyancy. The cells may be of uniform or varying size. A section of this film is extremely versatile in that any number of individual cells containing the same or different chemicals can be cut or torn from a larger piece of film allowing the user to control the desired dose of chemical. Solid product form packaging amounts typically range from about 0.1 g to about 1 kg, preferably from about 0.1 g to about 500 g. Liquid product form packaging amounts range from about 1 mL to about 1 L, preferably from about 1 mL to about 500 mL. Perforations between groups of air cells or individual air cells allow the desired doses to be torn off easily (Figure 3). Small doses of a chemical packaged in a perforated sheet of sealed cells would be particularly attractive for highly efficacious, low use-rate chemicals such as a pesticide (e.g., sulfonylurea herbicides). The large volume of chemical required for some high use-rate pesticides make their incorporation into a filled-cell package less desirable. In these cases, a bag is preferred.

(3) A third package type of the present invention is a filled-laminate package, used herein to denote a sheet of water-soluble polymer film laminated to a sheet of water-soluble cellular-air film on one or both sides from which the air cells protrude (Figure 4). The edges of the laminate are sealed thereby creating a closed space between the air cells which can be filled with chemical. If the air cells protrude from both sides of the cellular-air film, then two sheets of flat film can be laminated to the film, one on each side, to form a double laminated sheet.

(4) A fourth package type of the present invention is a filled film, used herein to denote cellular-air water soluble film in which one or more chemicals are incorporated into the polymer matrix of the sheet(s) forming the film.

The present invention further comprises combinations of the above types of packages. The cellular-air water-soluble film packages described above can contain multiple chemicals or compositions which are physically separated from one another in a single water-soluble package. Agricultural tank mix partners are ideal candidates for this type of packaging. Packages or combinations of packages of the present invention are especially advantageous for delivering a combination of distinct chemicals, which may be chemically or physically incompatible.

An example of such a packaging system is a cellular-air water-soluble film which contains at least one solid chemical in the air cells manufactured in the form of a bag which contains a liquid or gel chemical. This design can be reversed such that the air cells contain a liquid or gel chemical and the bag encloses a solid chemical. A second multiple-chemical or multiple-composition packaging design comprises a water-soluble film containing a chemical uniformly dispersed in the polymer matrix of the sheets forming the film (i.e., filled-film), which is subsequently fashioned into a cellular-air film into which one or more distinct chemicals can be contained in the air cells. One variation of this design is to encapsulate two or more different product forms in alternate rows or groups of air cells. Alternatively, a filled-film containing at least one chemical can be configured into a bag which is filled with a distinct chemical; or into a filled laminate package containing at least one chemical in one or more air cells, or in one or more void spaces between the air cells.

Furthermore, a package of the present invention can deliver three or more chemicals in a single package. Cellular-air filled-film containing one or two chemicals can be manufactured into a bag or filled-

laminated package in which is contained additional chemicals or compositions. For example, one chemical can be dispersed in the polymer matrix of the sheets forming the film (filled film), a second (or plurality of chemicals) can be encapsulated in the air cells of a cellular-air film formed from the filled-film, and a third can be contained by a bag fabricated from the filled-cell filled film. The filled laminate packages of the present invention can accommodate a plurality of distinct chemicals or compositions. One or more distinct chemicals can be contained within the air cells, one or more additional chemicals in the void spaces between the air cells, or a combination thereof. If a bag is fabricated from a filled laminate film, an additional chemical can be contained within the bag. If the filled laminate package is prepared from filled film, additional chemicals can be contained within the polymer matrix of the sheets forming the filled laminate package.

The packages of this invention contain enough air in the discrete cells or within the package to provide buoyancy in water or other aqueous liquids. The term "buoyancy" as used herein includes both positive buoyancy (floating at the surface) and neutral buoyancy (immersed or suspended in the liquid medium but neither sinking or rising). These packages remain suspended in the liquid medium or at its surface, where they may experience sufficient agitation to dissolve and disperse the product contents, and are kept away from any pump intake or other mechanical means attached to the vessel containing the liquid. The air keeps the package buoyant long enough for the aqueous medium and any agitation present to dissolve the film so that the chemical is released down through the aqueous medium. This buoyancy is especially advantageous in agricultural applications, such as use in spray tanks.

In addition, the air-containing cells also provide cushioning which protect the package from breakage during shipping and handling, thereby reducing the risk of worker exposure to any chemical contents.

5 In summary, the packages of the present invention provide the following advantages:

- 1) When delivering chemical to a vessel containing an aqueous medium, packages remain buoyant and will not block intake ports or  
10 openings at the bottom of the vessel;
- 2) Prevention of concentration of chemical at a single location within the vessel;
- 3) Reduction of risk of chemical leakage or  
15 breakage of contents due to the shock absorbing effect of the cellular-air;
- 4) Packaging is convenient to user by being easily disposable by dissolution in water or an aqueous medium thereby resulting in less  
20 of an adverse impact on the environment in that disposal in land-fills is not required;
- 5) Control of dosage of chemical is provided via packaging in perforated units; and
- 6) Packaging of several chemicals in a single package is possible.

25 The air volume for the packages and film of the present invention (provided by the cells or contained within a container fabricated from the film of the present invention) should be sufficient (1) to keep the package suspended or buoyant in the liquid prior to the  
30 release of the chemical product(s), said air volume typically being 5-50%, preferably 5-25%, of the total volume of the delivered chemical, and (2) to cushion the package and prevent it from rupture during shipping and handling. The exact volume of air necessary for  
35 buoyancy depends on the density of the chemical in the packaging, the downward suction force created by any

pump in the vessel, such as in a spray tank, and other factors specific to each use situation. Additional air, above that which is sufficient for buoyancy, can be provided by the cellular-air film to aid in  
5 additional cushioning and protection of the integrity of the bag, and prevent leakage during shipment and handling.

As previously noted, many different classes of chemicals are suitable contents for the film and  
10 packages of the present invention. In particular, agricultural chemicals which are suitable contents for the film and packages of the present invention include pesticides such as herbicides, fungicides,  
15 insecticides, nematocides, bactericides, acaricides, biological pest control agents, and plant growth regulators, as well as spreader-stickers, adjuvants, fertilizers, tank mix aids (e.g., defoamers), etc. The chemical can be in the form of liquids (excluding water), gels, water-dispersible granules, wettable  
20 powders or tablets. In short, any chemical compatible with the film can be packaged using the cellular-air water-soluble film or packages of the present invention, provided that the chemical does not dissolve the water-soluble packaging.

25 Examples of suitable agricultural pesticides include: Herbicides such as acifluorfen, asulam, atrazine, bensulfuron methyl, bentazon, bromacil, bromoxynil, hydroxybenzotrile, chloramben, chlorimuron ethyl, chloroxuron, chlorsulfuron,  
30 chlorotuluron, clomazone, cyanazine, dazomet, desmediphan, dicamba, dichlorbenil, dichlorprop, diphenamid, dipropetryn, diuron, thiameturon, fenac, fenuron, fluometuron, fluridone, fomesafen, glyphosate, hexazinone, imazamethabenz, imazaquin, imazethapyr,  
35 ioxynil, isoproturon, isouron, isoxaben, karbutilate, lenacil, MCPA, MCPB, mefluidide, methabenzthiauron,

methazole, metribuzin, metsulfuron methyl, monuron, naptalam, neburon, nitralin, norflurazon, oryzalin, perfluidone, phenmedipham, picloram, prometryn, pronamide, propazine, pyrazon, rimsulfuron, siduron, 5 simazine, sulfometuron methyl, tebuthiuron, terbacil, terbuthylazine, terbutryn, triclopyr, 2,4-D, 2,4-DB, triasulfuron, tribenuron methyl, primisulfuron, pyrazosulfuron ethyl, N-[[4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]-3-(ethylsulfonyl)-2-10 pyridinesulfonamide, nicosulfuron, and ethametsulfuron methyl; fungicides such as carbendazim, thiuram, dodine, chloroneb, cymoxanil, captan, folpet, thiophanate-methyl, thiabendazole, chlorothalonil, dichloran, captafol, iprodione, vinclozolin, 15 kasugamycin, thiadimenol, flutriafol, flusilazol, hexaconazole, and fenarimol; bactericides such as oxytetracycline dihydrate; acaricides such as hexathizox, oxythioquinox, dienochlor, and cyhexatin; and insecticides such as carbofuran, carbyl, 20 thiodicarb, deltamethrin, and tetrachlorvinphos.

The water-soluble sheets used in the films and packages of the present invention can be made by either casting from a resin solution and drying or by melt extrusion as described in U.S. 4,156,047.

25 The water-soluble polymer sheets can be manufactured into a cellular-air film packaging material as described for water-insoluble films in U.S. 3,142,599. U.S. 3,142,599 describes a method for the fabrication of an improved cushioning material 30 wherein at least one film layer is formed to provide a plurality of discrete air cells, and then a second or lidding layer is hermetically sealed to the first formed layer to seal the elements and thereby provide sealed cells in which air or another fluid is 35 entrapped.

Water-soluble cellular-air film of the present invention can also be made as described hereinafter. Inside a vacuum chamber, a water-soluble polymer sheet is drawn onto a moulding plate which contains negative  
5 depressions or recesses on it, in a pattern which will determine the depth and shape of the air cells. The air capacity of each cell can be controlled by the size and depth of the depressions on the moulding plate used to form the air cells on the film's surface.

10 At the bottom of each depression is a tiny orifice which allows a vacuum to be pulled against the polymer sheet evacuating all of the air between the sheet and the mold. An infrared heat source is applied to soften the sheet so that while it is under vacuum it will be  
15 pulled downward to fill the shape of each depression. Next, a face sheet or lidding sheet is drawn across the depression sheet and a heated roller seals the two sheets together to encapsulate air into the formed recesses. Heat sealing the face sheet occurs from  
20 about 25° to about 250°C with applied roller pressure in the range of  $2.07 \times 10^4$  to  $4.13 \times 10^4$  Pa. This is a continuous process where multiple layers of sheets are heated, thermoformed and fused together to form a single piece of cellular-air film. No air cells are  
25 positioned on the edges of the film so that a true airtight weld can be formed if the cellular-air film is intended to be welded into bags.

Another method, plug forming, rolls a heated embossing wheel or roller bearing a pattern of striking  
30 spikes across the polymer sheet, depressing the sheet into matched recesses on a moulding plate. This mechanical action presses the shapes of the air cells into the film. Another flat roller hermetically seals the face sheet or lidding sheet over the embossed sheet  
35 to encapsulate air in the recesses. This method also runs as a continuous process.



A third method for preparing cellular-air water-soluble film is to liquid cast a polymer resin over a form which contains a pattern of raised bumps on its surface. The raised bumps are the shapes which will  
5 determine the positioning and shape of the air cells on the film surface. A face sheet is heat sealed on top of the cured cast depression sheet in another step.

The cellular-air filled-films can be prepared in the following manner. The concept of delivering a  
10 single agricultural chemical in a flat water-soluble polymer is disclosed in U.S. 3,299,506 and British Patent 2,095,558. Each of these patents disclose a water-soluble polymer containing a uniformly dispersed chemical. The water-soluble polymer containing a  
15 chemical is formed into a thin flat film which can be torn or cut into measured sections for delivery of the chemical contained in the water-soluble polymer.

The water-soluble polymer film encapsulating agricultural chemical is made by dissolving the polymer  
20 being used in water followed by addition of and mixing of the agricultural chemical therewith and removal of water to form a solid polymer film with agricultural chemical dispersed therein. If the chemical is a liquid, it is added directly to the dissolved polymer.  
25 The combination results in an oil-in-water emulsion. A low-melting waxy solid agricultural chemical is heated above its melting point and added to the polymer solution. The polymer solution temperature and oven temperature are adjusted to a temperature that will  
30 ensure that the active ingredient does not decompose during processing. A powder can be added directly to the polymer solution or by making a slurry in water and adding it to the polymer solution. The combination results in a dispersion.

35 The resultant water-soluble filled film can contain from 1-75% of an agricultural chemical based on the

weight of polymer plus agricultural chemical, to provide the amount of chemical desired for particular application while still having desired film physical properties.

5       The mixture of dissolved polymer and agricultural chemical is cast into a film and then processed as described above to incorporate cellular-air. The water-soluble filled-film is drawn onto a moulding plate containing negative depressions (recesses) and  
10 then heat sealed to a face sheet. The plug forming method of rolling the heated embossing wheel bearing striking spikes across the film, and then hermetically sealing the face sheet over the embossed sheet to encapsulate air into the cells can also be used.  
15 Alternatively, the polymer resin containing the agricultural product can be liquid cast over a form which contains a pattern of raised bumps on its surface, and then heat sealed with a face sheet as described above. In all of these processes, the heat  
20 required for sealing and embossing is sufficiently low to prevent decomposition of the agricultural chemical in the film.

In the above processes, a liquid, solid or gel chemical to be contained in one or more air cells of a  
25 package is placed in such air cells prior to the sealing of the face sheet.

The cellular-air film with or without chemicals in the air cells can then be fabricated into a bag or envelope, for example by using a vertical form-fill-  
30 seal packaging machine as known in the art. A layer of cellular-air water-soluble film is wrapped around a tubular filling tube. The flat edges of the film are overlapped and a vertical weld is made by administering an electronic heat pulse which forms a vertical seam.  
35 The bottom of the tube is sealed with a transverse weld. The tubular film can then be filled with the

desired volume of chemical (liquid or solid). The filled section is pulled downward and off the form filling tube, and a second transverse weld is administered to seal the bag portion. This weld is large enough to form, when cut, the top of the filled bag and the bottom of the next bag to be filled. The cellular-air film can be positioned so that the air cells reside on the inside or outside of a finished envelope by positioning the film accordingly before it is welded into a tube.

The packages wherein the air cells are partially filled with a chemical are prepared in the following manner. One of the polymer sheets is treated as described above for the preparation of the cellular-air film to form a plurality of depressions. One or more of the depressions are then partially filled with the desired product, for example by a row of filling tubes. A second polymer sheet is heated to its fusing temperature and then pressed onto the filled sheet to form a unitary structure. The resulting filled-cell package contains one or more individually sealed cells containing a chemical product.

A filled-laminate package is made in the following manner. Water-soluble cellular-air film, containing at least one chemical encapsulated in one or more air cells, is made first as described previously. Then, a third sheet of polymer is rolled and heat sealed on top of the air cells. The outer edges on three sides of a film portion are welded together as described above, and the space inside the package (i.e., around the air cells and sandwiched between the flat sheets) is filled with a chemical. A second transverse weld is administered to seal the fourth outer edge of the filled-laminate (see Figure 4).

The cellular-air water-soluble film and packages of the present invention have utility in many areas of packaging and shipping. For example, it can be used:

- 5           1) As a disposable wrap for perishable foods, such as fruits, nuts, grains, etc. where prevention of insect egg laying, insect consumption, bruising spoilage, and fungal attack is desirable during shipment;
- 10          2) In the mold making/casting process for non-aqueous low-melting materials. A positive impression can be formed by incorporating the water-soluble cellular-air shape into the mold.
- 15          3) As a general purpose, disposable biodegradable cellular-air wrap for use in the packaging, shipping industry (e.g., for calculators, stereos, china, appliances, and other fragile items).
- 20          4) For delivery of chemicals in the marine, fish farming, aquarium, swimming pool, water treatment, agricultural, pharmaceutical, research, or consumer industries or to any volume of water or aqueous liquid.
- 25          5) For delivery of chemicals to municipal water-purification systems or individual septic systems.

Perhaps the broadest use of this invention is for use as a disposable outer protective cushioning to safeguard delicate and fragile items during shipment. A packager may find it convenient to either roll flat  
30 pieces of water-soluble cellular air film around objects for cushioning or place them inside pre-formed heat sealed envelopes or bags fabricated from the film depending on their size, shape, and number. A flat piece of film for cushioning can be cut from a roll to  
35 the desired size. An object can then be rolled up inside the wrap which is then secured to itself with a

piece of adhesive tape or by other means.

Alternatively, an object may slide easily inside a pre-formed heat sealed envelope or bag which is slightly larger than the object it contains. Flat pieces of the film for cushioning may also be used as separation layers between items which stack well such as dishes. Below are numerous examples of objects for which a protective outer covering of the water-soluble cellular air film of the present invention may be useful for cushioning.

Objects which may benefit from outer protection with the film or packages of the present invention during shipment are:

- 1) Delicate items such as glassware, ceramics, china, crystal, porcelain collectibles;
- 2) Scientific supplies such as precision gauges, glass thermometers, microscope lenses, hand magnifiers, lab glassware, pH probes, and other delicate instruments;
- 3) Camera equipment and accessories such as lenses and filters;
- 4) Electronic equipment such as radios, remote controls, calculators, telephones, computer components, and small replacement parts;
- 5) Light bulbs for industry, home, auto, and hobby applications;
- 6) Lighting lenses and globes for light fixtures; and
- 7) Framed art, statuary, plaques, and engravings.

Disposal of the film and packages of the present invention is via dissolution in water or an aqueous medium. The fact that disposal in a land-fill is not required provides an environmental advantage.

In the Examples hereinafter, the water-soluble film used was Chris\*Craft® M8533, a 38 micron thick flat water-soluble film. It is cold-water soluble with a

disintegration time of 35-40 seconds at temperatures of 5°C. An aluminum Die Press Block was used to form the air cells. The Die Press Block consisted of matched male-female die partners. A heated Carver Laboratory Press was used to collapse the die together and press the air cell shapes into the sandwiched film.

#### EXAMPLE 1

This Example illustrates the preparation of the cellular-air film. A 12.7 x 12.7 cm piece of 38 micron M8533 film was taped over the hole area of the female die plate. Carver Lab Press plates were heated to approximately 75°C. The male die plate was positioned on top of the female die plate using alignment pins. The opposed die plates with film sandwiched in between were placed on the Carver Lab Press. The die plates were pressed together hydraulically for 30 seconds with an applied pressure registering  $6.9 \times 10^5$  to  $13.8 \times 10^5$  Pa. The die block was removed from the press and opened. Negative depressions (diameter = 0.6 cm, depth = 0.6 cm) were pressed into the originally flat film. The masking tape was removed and a second 12.7x12.7 cm piece of flat film to serve as the lidding layer was positioned on top of the layer with the thermoformed depressions. A 15.2x15.2 cm piece of flat aluminum was positioned on top of the film layers. The die block was again pressed between heated press plates (105°C) of a Carver Lab Press for 30 seconds at an applied pressure of  $13.8 \times 10^5$  to  $34.5 \times 10^5$  Pa. The die block was removed from the press and 10.2x12.7 cm section of cellular-air film was removed. The resulting section of film had encapsulated air cells on the film surface, each cell having a diameter of 0.6 cm and a height of 0.6 cm. The cells contained only air.

#### EXAMPLE 2

This Example describes the encapsulation of solid product in the air cells. Negative depressions were

formed in a 12.7x12.7 cm flat piece of 38 micron M8533 film as described in Example 1. The die block was pressed between heated press plates (80-87°C) for 30 seconds at an applied pressure of  $137.9 \times 10^5$  Pa. The die block was removed from the press, opened, and the masking tape was removed. Approximately 0.1 g of Ally® 60DF sulfonylurea herbicide was added to each of the thermoformed negative depressions. A second layer of film was placed over the filled depressions, and then it was covered with a solid 15.2x15.2 cm aluminum plate. The die block was again pressed between heated press plates (140°C) for 1 minute at an applied pressure of  $137.9 \times 10^5$  Pa. The die block was removed from the press and opened. The resulting section of film had encapsulated air cells each containing the solid product in discrete gum-drop-shaped cells (diameter = 0.6 cm, height = 0.6 cm).

### EXAMPLE 3

This Example describes the preparation of a cellular-air bag. For test purposes, propylene glycol, an organic liquid, was used as the bag contents instead of an actual agricultural product. However, a liquid agricultural product or formulation would work equally well in the packaging of this Example.

Two finished 10.2x12.7 cm sheets of cellular-air film were prepared by the procedure described in Example 1. The heated Carver Lab Press plates (120-130°C) were used at an applied pressure of  $344.7 \times 10^5$  Pa to collapse the die block between the press plates during the depression forming and lidding steps for both sections of film. The two sheets of cellular-air film were pressed on top of one another with the smooth sides on the inside and the gum-drop-shaped air cells facing outward. Three sides were impulse heat sealed to form an open-ended bag. The unfilled cellular-air bag was trimmed to measure

10.2x10.2 cm. The liquid, 88 g of yellow dyed propylene glycol, was poured into the bag. The fourth side was impulse sealed to form a finished bag measuring 8.9x10.2 cm and weighing 91.72 g. Each side  
5 of the bag contained 50 air cells. Approximately 17 mL of air was contained by the 100 air cells on the bag surface. The volume of cellular air was approximately 20% of the volume of the bag's liquid contents.

EXAMPLE 4

10 A small calculator, measuring 12.5 mm in thickness, 7.6 cm in width, and 14 cm in length is placed inside an open ended envelope measuring 11.5 cm wide by 18 cm long. The envelope is formed by folding a 23 cm by  
15 36 cm flat sheet of 3 mil thick water-soluble cellular air cushioning into the shape of a cylinder. The longitudinal edge and bottom edge are impulse heat sealed together just below the melting point of the polymer while under pressure to form an open-ended  
20 11.5 cm by 18 cm envelope. Each side of the envelope has 18 rows of air cells, 9 air cells per row in a close spacial arrangement. Each air cell measures  
25 9.5 mm in diameter by 3.1 mm in height. Air cells face out from the envelope, cushioning the calculator contained inside. The open end or top of the envelope is folded over and secured shut with a piece of adhesive tape.

EXAMPLE 5

A stack of 12 china dinner plates each measuring 10 inches in diameter is cushioned for shipment by  
30 placing a 30.5 cm square flat sheet of 3 mil thick water-soluble cellular air cushioning film in between each plate. Approximately, eight hundred air cells each measuring 9.5 mm in diameter by 3.1 mm in height are arranged in 33 rows, 24 per row, on the surface of  
35 the water-soluble cellular air cushioning material. A piece of the same cushioning material measuring 1 meter



by 30.5 cm is used to surround the stack of dinner plates, secured in place with adhesive tape.

What is claimed is:

1. A film comprising a water soluble polymer sheet having one or more discrete air cells on its surface.
2. A film of Claim 1 further comprising a plasticizer.
3. The film of Claim 1 wherein the polymer comprises polyvinyl alcohol; vinyl alcohol copolymers; polyethylene oxide; substituted cellulose; starch; gelatin; polyvinyl pyrrolidone or polyvinyl pyrrolidone copolymers; copolyesters of hydroxyvaleric acid and hydroxybutyric acid; copolymers of ethylene and acrylic acid; or copolymers of ethylene and methyl acrylic acid.
4. The film of Claim 1 wherein said air cells contain air and at least one chemical.
5. The film of Claim 4 wherein the air in the cells equals from about 5% to about 50% by volume of the delivered chemical.
6. The film of Claim 1 wherein the water soluble polymer sheet contains at least one chemical dispersed within the polymer sheet.
7. The film of Claim 6 wherein the water soluble polymer sheet is perforated between at least two discrete groups of air cells, or between each air cell.
8. The film of Claim 1 in the configuration of a container.
9. A package for delivering agricultural chemicals comprising:
  - 1) a film of a water soluble polymer sheet having one or more discrete air cells on its surface containing air equal to from about 5% to about 50% by volume of a delivered chemical, and
  - 2) at least one agricultural chemical.

10. The package of Claim 9 wherein air and the agricultural chemical is contained within a container fabricated from the film.

5 11. The package of Claim 9 or 10 wherein air and the agricultural chemical is contained within at least one of the air cells.

12. The package of Claim 9 or 10 wherein the agricultural chemical is dispersed within the polymer sheet.

10 13. The package of Claim 11 wherein the agricultural chemical is dispersed within the polymer sheet.

14. A package for delivering agricultural chemicals comprising one or more laminates of

- 15 1) a first film of a water soluble polymeric sheet having one or more discrete air cells on its surface,
- 2) a second film of a water soluble polymer sheet of the same or different
- 20 composition laminated to the first film on one or both sides from which the air cells protrude, and
- 3) at least one agricultural chemical said laminate having a total amount of air in the cells
- 25 equal to from about 5% to about 50% by volume of the delivered chemical.

15. A package of Claim 14 wherein at least one agricultural chemical is contained in the spaces between the first and second films around the air

30 cells.

16. A package of Claim 14 or 15 wherein at least one agricultural chemical is independently dispersed within either polymer sheet.

17. A package of Claim 14 or 15 wherein at least

35 one agricultural chemical is contained in at least one of the air cells.

18. A package of Claim 16 wherein at least one agricultural chemical is contained within at least one of the air cells.

5 19. A package of Claim 14 wherein air and the agricultural chemical are contained within a container fabricated from the laminate.

20. A package of Claim 19 wherein an agricultural chemical is also contained within the spaces between the first and second films around the air cells.

10 21. A package of Claim 19 wherein an agricultural chemical is also contained in at least one of the air cells.

22. A package of Claim 19 wherein an agricultural chemical is also dispersed within either polymer sheet.

15

1/1

FIG. 1

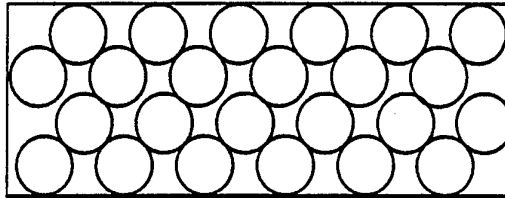


FIG. 2

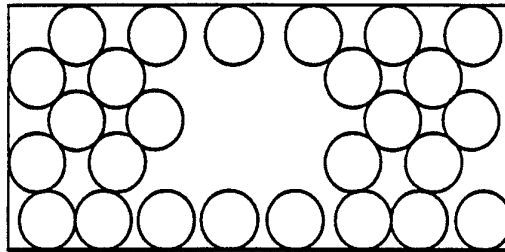


FIG. 3

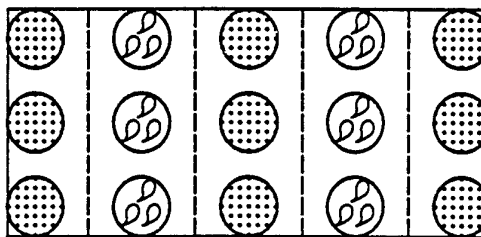
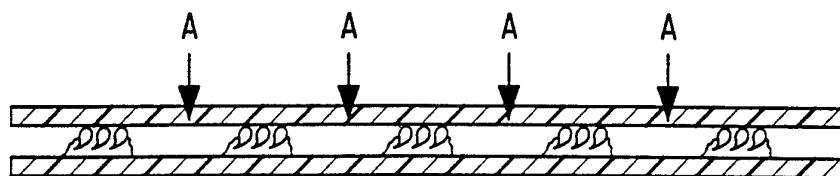


FIG. 4



INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 93/06565

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 5 B65D65/46 A01N25/34

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 5 B65D A01N

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR,A,2 342 027 (DEUTSCHE GESELLSCHAFT FUR SCHADLINGSBEKAMPFUNG M.B.H.) 23 September 1977	1,3-5,9, 11
A	see the whole document ---	14,17
X	EP,A,0 244 084 (BALL) 4 November 1987	1,4,5,9, 11
A	see the whole document ---	7,14,17
Y	US,A,4 156 047 (WYSONG) 22 May 1979 cited in the application	1-3,6, 8-10,12
A	see the whole document ---	14
Y	US,A,3 142 599 (CHAVANNES) 28 July 1964 cited in the application	1-3,6, 8-10,12
A	see the whole document ---	14
	-/--	

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

\* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*&\* document member of the same patent family

Date of the actual completion of the international search

9 November 1993

Date of mailing of the international search report

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,  
Fax (+ 31-70) 340-3016

Authorized officer

LEONG, C

## INTERNATIONAL SEARCH REPORT

Internat. Application No.

PCT/Us 93/06565

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	GB,A,2 095 558 (AVON PACKERS) 6 October 1982 cited in the application	1-3,6, 8-10,12
A	see the whole document ---	16
A	US,A,3 695 989 (ALBERT) 3 October 1972 see the whole document -----	1,3,8-10

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 93/06565

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR-A-2342027	23-09-77	DE-A- 2607638	01-09-77
		AU-B- 508652	27-03-80
		AU-A- 2210077	17-08-78
		CA-A- 1074734	01-04-80
		JP-C- 1160442	10-08-83
		JP-A- 52120130	08-10-77
		JP-B- 57054104	16-11-82
-----	-----	-----	-----
EP-A-0244084	04-11-87	NONE	
-----	-----	-----	-----
US-A-4156047	22-05-79	US-A- 4119604	10-10-78
		AT-B- 359285	27-10-80
		AU-B- 508102	06-03-80
		AU-A- 2797377	22-02-79
		BE-A- 882471	16-07-80
		BE-A- 882472	16-07-80
		BE-A- 882473	16-07-80
		CA-A- 1102470	02-06-81
		CH-A- 629835	14-05-82
		DE-A- 2737339	23-02-78
		FR-A, B 2362187	17-03-78
		GB-A- 1579753	26-11-80
		JP-A- 53024351	07-03-78
		LU-A- 77987	27-04-78
		NL-A- 7709157	21-02-78
		SE-B- 420317	28-09-81
SE-A- 7709269	19-02-78		
US-A- 4155971	22-05-79		
-----	-----	-----	-----
US-A-3142599		NONE	
-----	-----	-----	-----
GB-A-2095558	06-10-82	NONE	
-----	-----	-----	-----
US-A-3695989	03-10-72	NONE	
-----	-----	-----	-----