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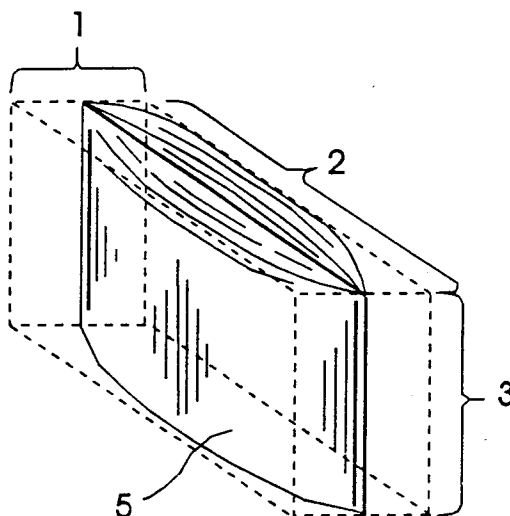
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F-69263 Lyon Cedex 09 (FR)(54) **Hazardous chemical shipping container.**

(57) The invention relates to a containerization system suitable for containing water soluble or dispersible packages where the package is placed in a rigid outer container the inner dimensions (1,2,3) of which are equal to or smaller than the width perimeter and length perimeter of the bag (5) respectively.

FIG. 1**EP 0 631 947 A1**

FIELD OF THE INVENTION

The inventor relates to a containerization system suitable for containing water soluble packages of Hazardous materials comprising a rigid packing container wherein the total width-length outer perimeter of the water soluble package is equal to or less than the corresponding inner width perimeter in the container into which it is placed.

BACKGROUND OF THE PRIOR ART

At the present the introduction of Hazardous materials such as agrochemicals especially in the form of gels in flexible water soluble packages has commenced. These are shown to be useful because they can be handled with relative ease without significant difficulties and without danger of contact with the bag's contents. In U.S. Patent 5,080,226 agrochemicals in water soluble bags are described. These are in the form of gels in flexible polymer water soluble bags. They represent an improvement over prior bags because of the improvements in the prevention of leakage and spilling in such bags during transportation, handling, and storage. While these bags represent a major step forward in the use of such containers, flexible containers are difficult to ship and are usually placed in a shipping container. Normally for shipments in a container, certain strength requirements must be met. U.S. Government regulations require that the drop and damage resistance of the contents in a shipping container must stop the product from leaving the shipping container, see Govt. Reg. 49 C.F.R. 178.516, 49 C.F.R. 178.603, and the transport of dangerous goods 9.7.3. In addition the package must be subjected to such drop at 1.2 meters -8°C because this condition could exist in the real world. The colder the ambient temperature is, the more brittle polymeric bags normally are and more difficult to perform the test successfully.

Normally, rigid containers are used in shipping and handling of hazardous materials to allow shipment of multiple units and to give further protection to the contents. For example, corrugated boxes, normal design of such rigid containers is to design a cavity for placement of the contents where all three dimensions are slightly to greatly bigger than the contents to be shipped. Smaller containers, having one or more dimensions smaller than the contents, while more cost effective, are not used because of the difficulty of insertion, problems with fit, and the tendency of a smaller container to transmit more shock and in general be less protective than a larger container.

It also can be a problem when placing the polymeric bags in a rigid container for shipment that the corners of the bags dry out, crack, or otherwise leak on storage or on high impact. In other words, current box design does not tend to further reduce failure rather it tends to increase it. It would be useful if a shipping container could be designed which improved the storage and shipping parameters of such water soluble containers.

SUMMARY OF THE INVENTION

It is a main object of this invention to provide a containerization system for storage and transportation of water soluble Hazardous chemical products which improves the storage and shipping resistance to breaks and leaks. The present invention addresses the problems of prior containers. The present invention is directed to a containerization system comprising:

- a) A water soluble or water dispensable bag which completely encloses a hazardous chemical or agricultural chemical;
- b) a rigid outer container for containing said bag wherein the bag length perimeter is greater than or equal to the corresponding inside perimeter of the rigid container which contacts the bag length perimeter and the bag width perimeter is greater than or equal to the corresponding inside perimeter of the rigid container which contacts the bag width perimeter.

In preferred embodiments the rigid container can contain a plurality of said bags wherein the wall of one adjacent bag forms the perimeter wall for enclosing the other bag (See Fig. 2).

It is a further object of this invention to provide a new method and containerization system for packaging hazardous chemicals.

Another object is to provide a new system which is easy to manipulate by the end user and manufacturer. Another object is to provide new containerization systems which diminish risks of leakage, pollution, and contamination. Another object of the invention is to protect any water insoluble bags used to enclose the water soluble bag from breaking.

Yet another object is to dissipate the force of a shock away from the water soluble bag when transporting said bags.

A further object is to provide a container which is a cost savings advantage in both shipping and manufacturing. Other objects will be clear to those skilled in the art from the description, Figures, and Examples which follow and all may be achieved in full or part using the invention.

5 **DESCRIPTION OF THE FIGURES**

Figure 1 is a view of a containerization system of the invention comprising single bag in a rigid container.

Figure 2 is a view of a containerization system of the invention comprising 2 bags in the rigid container
10 where the wall of one bag forms a wall containing other bag.

Figure 3 is a longitudinal view of a bag sitting on a level surface with arrows indicating the bag length perimeter.

Figure 4 is a view of the side of the bag on a level surface with arrows indicating the bag width perimeter.

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DESCRIPTION OF THE PREFERRED EMBODIMENTS

The system of the present invention comprises a water soluble or dispersible bag enclosing a hazardous chemical. The bag is further contained in a rigid outer container wherein the outer length
20 perimeter of the bag is less than or equal to corresponding inner perimeter of the rigid container and the outer width perimeter of the bag is less than or equal to the corresponding inner perimeter of the container.

By "water soluble or water dispersible bag enclosing a hazardous chemical" is meant the distribution and containerization system, for example, in U.S. Patent 5,080,226. This type of system comprises a water soluble or dispensable enveloping film preferably soluble in cold water and a Hazardous chemical.

25 The chemical nature of the enveloping film constituting the bag can vary quite widely. Suitable materials are water soluble (or possibly water dispersible) materials which are insoluble in the organic solvents used to dissolve or disperse the active ingredient (e.g., agrochemical). Specific suitable materials include polyethylene oxide, such as polyethylene glycol; starch and modified starch: alkyl and hydroxyalkylcellulose, such as hydroxymethylcellulose, hydroxyethylcellulose, hydroxypropyl cellulose: carboxymethylcellulose: polyvinylethers such as poly methyl vinylether or poly(2-methoxyethoxyethylene); poly(2,4-dimethyl-
30 6-triazinylethylene; poly(3-morpholinyl ethylene); poly(N-1,2,4-triazolylethylene); poly(vinylsulfonic acid); polyanhydrides; low molecular weight melamine-formaldehyde resins; low molecular weight urea formaldehyde resins; poly(2-hydroxyethyl methacrylate); polyacrylic acid and its hohlogs.

A preferred enveloping film comprises or is made from polyvinylalcohol (PVA). When PVA is used, it is
35 preferably partially or fully alcoholized or hydrolyzed, e.g., 40-100%, preferably 80-99% alcoholized or hydrolyzed, as a polyvinyl acetate (or other ester) film. Copolymers or other derivatives of such polymers can also be used.

Additional preferred materials for constituting the bags in the invention are polyethylene oxide, methylcellulose, and polyvinylalcohol.

40 A hazardous chemical can be any compound which can easily cause extreme injury to persons exposed to the chemical or which can easily damage the environment. Examples are acids, bases, caustics, poisons, and agrochemicals. An agricultural chemicals or agrochemicals are compounds such as pesticides (e.g., herbicides, fungicides, nematocides, insecticides, etc.) and plant protection agents (e.g., plant growth regulators, nutrients, etc.). Agrochemicals also include plant adjuvants such as penetrating agents and the
45 like.

Hack's Chemical Dictionary, 5th Edition, says that Hazardous chemicals are chemicals that may cause loss of life or property by improper handling, shipping, or storing.

Those Hazardous chemicals or agricultural chemicals may be in any convenient form, for example, solid, liquid, or gel and are preferably water soluble or dispersible. Liquids and gels are preferred with gels
50 being especially preferred.

A gel is generally a colloid in which the dispersed phase has combined with the continuous phase to produce a viscous, jelly-like product. A gel can be a dispersed system consisting typically of a high molecular weight compound or aggregate of small particles in very close association with a liquid. The gels used in the invention usually have an organic continuous phase. Furthermore, the gels used in the invention
55 have essentially one physical phase, at least as can be seen when visually observed. Gels that are preferred for the invention are those which can be divided by cutting and whose cut parts are able to merge together by simple juxtaposition.

Solvents useful in the gel of the present invention are organic solvents such as petroleum hydrocarbons which include aliphatic and aromatic solvents. Surfactants that can be used in the invention are nonionic and anionic surfactants and combinations thereof. Illustrative gelling agents that can be used include mixtures of dioctyl sulfosuccinate salt and sodium benzoate, tetramethyl decynediol ethoxylated dialkyl-phenol, combinations of modified clay and propylene carbonate, hydrogenated castor oil, ethoxylated vegetable oil, dioctyl ester of sodium succinic acid and sodium benzoate, diatomaceous earth, and mixtures of dimethyl hexane and hexyne diol.

The gel material which is used in the invention is essentially a material which has a phase difference L between the controlled shear stress and the resulting shear strain such that $\text{tg}L$ is less than or equal to 1.5, preferably less than or equal to 1.2. $\text{Tg}L$ is the tangent of the L angle (or phase difference). The measurement of L is made by means of a rheometer having a flat fixed plate and a rotating cone above this plate such as the angle between them is less than 10° , preferably 4° . The cone is caused to rotate by means of a controlled speed motor; the rotation is a sinusoidal one, i.e., the torque and the angular displacement change as a sine function with time. This angular displacement corresponds to the hereabove mentioned shear strain; the torque of the controlled speed motor (which causes the angular displacement) corresponds to the hereabove mentioned controlled shear stress.

The gel which may be used in the invention is primarily organic, which means that it has a low water content, generally less than 5% (by weight), preferably less than 3%, more preferably less than 1%.

Generally, the gel which may be used in the invention is a material having a viscosity from 500 centipoise (measurement made with a Brookfield viscometer at 23°C , with a flat plate rotating at 20 round per minute) to 50,000 centipoise, preferably between 1,000 and 30,000 centipoise, and still more preferably between 1,000 and 5,000 centipoise.

According to one embodiment of the invention, the gels which are used in the invention are successful when submitted to the following puncture test: 500 g of a material/gel are placed in a polyvinyl alcohol water soluble bag (having a 50 micron thick wall) and heat sealed. The bag is suspended using a binder clip at which time a dissecting needle (the diameter of which is 0.1 mm) is inserted into the lower third of the bag and withdrawn. The material/gel is observed for 30 minutes to determine leakage. A gel which is successful in the present test shows no leakage and preferably may be used in the invention. A droplet of material may appear on the hole, but no persistent flowing or leaking occurs.

Preferred characteristics of a gel which is appropriate for the invention are (alone or in combination):

The viscosity should be generally between 500 and 50,000 centipoise, preferably between 1,000 and 30,000 centipoise, and still more preferably between 1,000 and 5,000 centipoise (measurement made with a Brookfield machine).

The dispersibility in water should be substantially complete when the gel is subjected to normal agitation in water after a 15-minute interval, preferably after a 10-minute interval.

The gel preferably contains an essentially nonaqueous solvent. According to another feature, the gels and the bag containing gel of the invention preferably have a density greater than 1, preferably greater than 1.1.

In practice, the Hazardous chemical used in the invention and is contained in the water soluble bag comprises the active ingredient, which is the hazardous chemical in association with ingredients that participate in or assist in the formation of the gel, for example, surfactants, dispersants, thickeners, solvents and gelled or gelling agents.

It is practical that the bag also be enclosed in an additional non-water soluble flexible bag. In the event of severe trauma which does break the bag the outer bag will help contain any leak.

By rigid containers, herein is meant those rigid containers normally used to ship product such as water soluble bags. These are normally made of corrugated board but can be made of plastic, metal, wood, or any other similar rigid material approved for use in the shipping trade.

The bag length perimeter is the measurement taken when a bag is placed on a flat level surface measuring entirely around the length of the bag both top and bottom. Figure 3 is a representative of a bag on a length view with the arrows indicating the perimetral length measurement. Likewise the bag width perimeter is the measurement taken when a bag is placed on a flat level surface measuring around the width of both top and bottom. Figure 4 is a representative of a bag width perimeter with arrows indicating the perimeter width measurement.

The "inside perimeter" is measured by using the inside measurements of the sides of the box in contact with the respective width and length of the bag. In Figure 1, 1 is a width, 2 length, and 3 is height. The perimeter corresponding to bag(s) length perimeter would be $2 \times (\text{length} + \text{width})$ while the

determination for the box dimensions in contact with the width would be $2 \times (\text{Width} + \text{Height})$. As an example then, where the bag had a width perimeter of 12 the box perimeter might be width 2.25 height 3.75 for a box perimeter of $2(2.25 + 3.75)$ or a perimeter of 12, the bag should have no more width perimeter than about 12. Likewise for the length perimeter.

Where desired a plurality of bags can be placed in a box of the invention. So for example in Figure 2 there are 2 bags in a single box. Either a divider may be placed between the 2 or the wall of one bag may form a wall of the inner perimeter of the rigid container for purposes of this invention. While that wall may not be as rigid as say corrugated board, it appears that the inner wall such as this can be used without detracting from the effectiveness of the invention. So in the drawing of Figure 2 dotted line 4 becomes a wall of both the first bag and second bag therein. Since the bags are flexible it is possible to fit bags with 2 dimensions bigger than the inner dimensions of the box with the contents of the bag shifting accordingly. Of course there is a physical limit to the difference which will become readily apparent to those skilled in the art upon applying the invention containerization system.

The following examples are representative of the invention and are not intended to be limiting. Other choices of materials, methods, sizes, and the like will be readily apparent to those skilled in the art on viewing the disclosure and examples.

EXAMPLES

Bags containing Buctril brand gel made according to U.S. Patent 5,080,226. They were enclosed in water soluble polyvinyl alcohol bags sealed and further placed in water insoluble outerwraps of a polyethylene type film. The films are wrapped tight around the bag.

The bags were then placed in various size corrugated boxes 2 to a box along the lines of Figure 2. The boxes were sealed and dropped from heights of 32", 47", and 71". Tests were done with boxes both within the invention and outside. In the following table are the results of boxes with 2 bags. Box dimensions are for the entire box and need to be halved where appropriate while bag dimensions are width and length perimeter. Failure represents a breach in the bag such that its contents begins to empty anywhere from pinhole to splits of the entire width or length of the bag. All bags had a width perimeter of 12" and a length perimeter of 24 inches.

	EX	CONT. LENGT H	CONT. WIDTH	CONT. HEIGH T	32" DROP	47" DROP	71" DROP	BOX PERIMETE R W	BOX PERIMETE R L
5	1	8.875	5.375	5	failure	no test	no test	15.375	23.125
	2	8.875	5.375	4.25	failure	no test	no test	13.875	23.125
	3	8.875	5.75	4	failure	no test	no test	13.75	23.5
10	4	8.875	5.75	3.75	failure	no test	no test	13.25	23.5
	5	10	5	4.5	failure	fail	no test	14	25
	6	10	5	4.25	no fail	fail	no test	13.5	25
	7	10	5	4	no fail	fail	no test	13	25
15	8	10	4.75	4.75	no fail	fail	no test	14.25	24.75
	9	10	3.75	4.25	no fail	fail	no test	12.25	23.75
	10	12	6	0	current	filled	bag	12	2
20	11							0	0
	12	9.75	3.75	3.75	no fit	no fit	no fit	11.25	23.25
	13	9.75	4	3.75	no fit	no fit	no fit	11.5	23.5
25	14	9.75	4.5	3.75	no test	no failure	no failure	12	24
	15	9.5	4.75	3.5	no test	no failure	no failure	11.75	23.75
	16	9.5	5	3.5	no test	no failure	no failure	12	24
	17	9.5	5.25	3.5	no test	7" + 4/9" + 9"	no test	12.25	24.25
30	18	9.5	5.5	3.5	no test	6" + Pinhole	9" + 6"	12.5	24.5
	19	9.25	5	3.25	no test	no failure	no failure	11.5	23.5
	20	9.25	5.25	3.25	no test	no failure	no failure	11.75	23.75
35	21	9.25	5.5	3.25	no test	no failure	no failure	12	24
	22	9.25	5.75	3.25	no test	no failure	no failure	12.25	24.25

40 Claims

1. A containerization system for shipping hazardous chemicals comprising
 - a) a water soluble or water dispersible bag which completely encloses a hazardous chemical; and
 - b) a rigid outer container containing said bag; wherein the bag length perimeter is greater or equal to the corresponding inside perimeter of the outer container and the bag width perimeters greater or equal to the corresponding inside perimeter of the outer container.
2. A containerization system according to Claim 1 wherein the hazardous chemical is a liquid or gel.
3. A containerization system according to Claim 2 wherein the hazardous chemical is a gel.
4. A containerization system according to Claim 2 wherein the rigid outer container is of corrugated board.
5. A containerization system according to Claim 2 wherein the bag length or width perimeter is equal to the corresponding inside perimeter of the rigid container.
6. A containerization system according to Claim 2 wherein the bag further comprises an insoluble outer wrap.

7. A containerization system according to Claim 2 wherein the bag length and width perimeter is greater than the corresponding inside perimeter of the rigid container.
- 5 8. A containerization system according to Claim 1 wherein the bag length and width perimeter is greater than the corresponding inside perimeter of the rigid container by no more than about 10%.
9. A containerization system according to Claim 2 wherein the bag length and width perimeter is greater than the corresponding inside perimeter of the rigid container by no more than about 5%.
- 10 10. A containerization system according to Claim 2 which comprises plurality of bags in a ridged container.
11. A containerization system according to Claim 2 which comprises 2 bags in a ridged container.
12. A containerization system for shipping agricultural chemicals comprising:
15 a) a water soluble or water dispersible bag which completely encloses an agricultural chemical; and
b) a rigid outer container containing said bag; wherein the bag length perimeter is greater or equal to the corresponding inside perimeter of the outer container and the bag width perimeters greater or equal to the corresponding inside perimeter of the outer container.
- 20 13. A containerization system according to Claim 12 wherein the agricultural chemical is a liquid or gel.
14. A containerization system according to Claim 13 wherein the agricultural chemical is a gel.
15. A containerization system according to Claim 13 wherein the rigid outer container is of cardboard.
25
16. A containerization system according to Claim 13 wherein the bag length or width perimeter is equal to the corresponding inside perimeter of the rigid container.
17. A containerization system according to Claim 13 wherein the bag further comprises an insoluble outer
30 wrap.
18. A containerization system according to Claim 13 wherein the bag length and width perimeter is greater than the corresponding inside perimeter of the rigid container.
- 35 19. A containerization system according to Claim 12 wherein the bag length and width perimeter is greater than the corresponding inside perimeter of the rigid container by no more than about 10%.
20. A containerization system according to Claim 13 wherein the bag length and width perimeter is greater than the corresponding inside perimeter of the rigid container by no more than about 5%.
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21. A containerization system according to Claim 13 which comprises a plurality of bags in a ridged container.
22. A containerization system according to Claim 13 which comprises 2 bags in a ridged container.
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FIG. 1

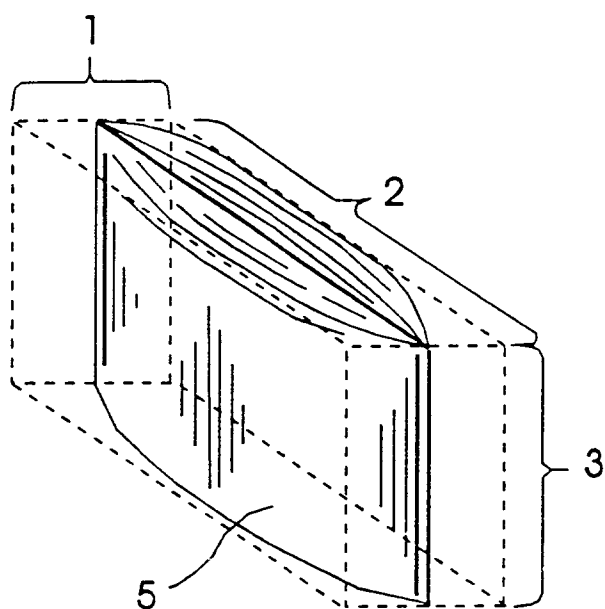


FIG. 2

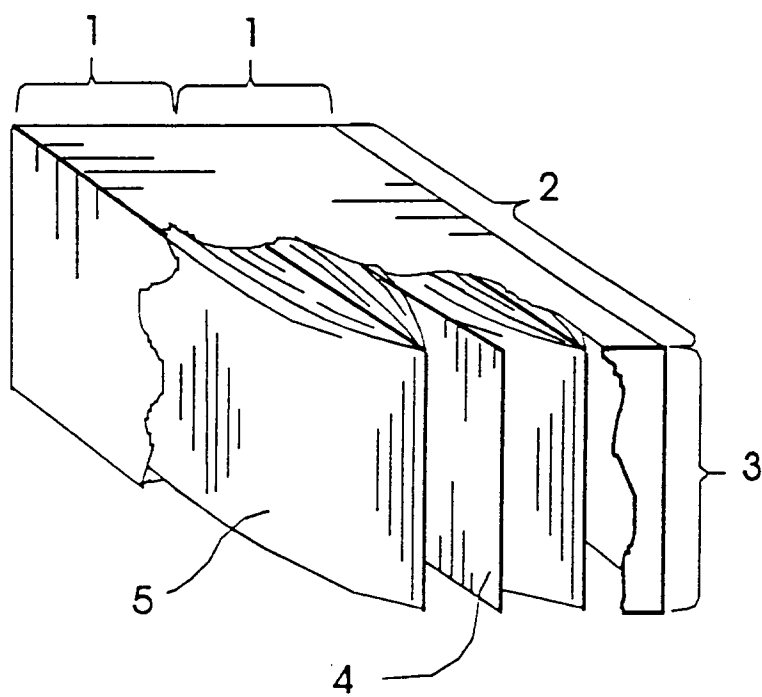


FIG. 3

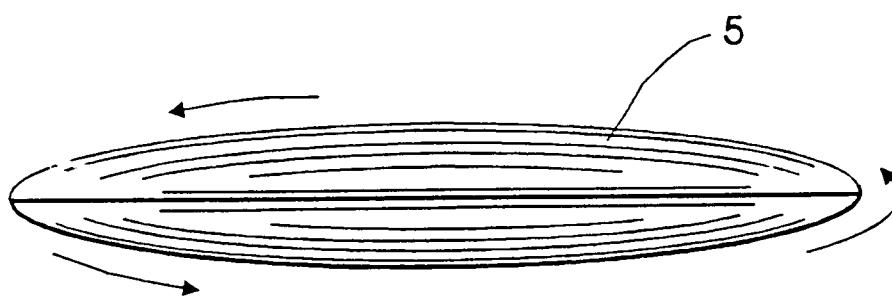
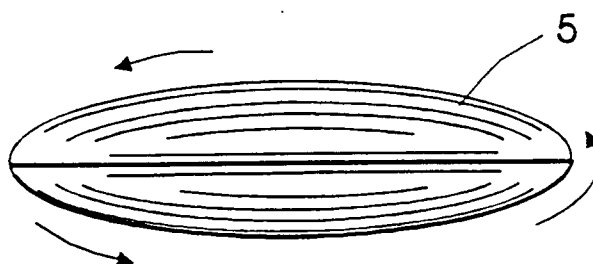


FIG. 4





European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 94 10 9692

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
Y A	WO-A-89 12590 (MAY & BAKKER LIMITED) * page 14, line 4 - page 15, line 13; figure 3 * ---	1,12 2,13	B65D77/06 B65D65/46
Y A	US-A-2 669 351 (C.M. CARSON ETAL) * column 3, line 46 - line 57; figures 3-6 * * column 3, line 10 - line 11 * ---	1,12 4,5, 7-11,15, 16,18-22	
A	EP-A-0 549 349 (RHONE-POULENC AGROCHIMIE) * claims 1,25 * ---	1-3,6, 12-14,17	
D,A	US-A-5 080 226 (LEONARD E. HODAKOWSKI ETAL) * column 3, line 56 - line 66 * ---	1-3, 12-14	
A	DE-A-29 15 228 (HENKEL KGAA) * page 13, line 1 - line 14; figure 1 * -----	1	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			B65D
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 15 September 1994	Examiner Deprun, M
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