AEROSOL DISPENSER WITH DIFFERENTIALLY PERMEABLE RECEPTACLES

Felix Rousselot, Liguge, France, assignor to Geigy Chemical Corporation, Ardsley, N.Y.
Filed May 16, 1967, Ser. No. 638,944
Claims priority, application France, May 16, 1966, 61,700
6 Claims. (Cl. 222—193)

ABSTRACT OF THE DISCLOSURE

A push-button dispensing apparatus, of the aerosol bomb type, for dispensing solid or liquid material in a finely-divided state, and comprising a product container containing the active agent to be distributed, a propellant cartridge within said product container and containing a liquefied propellant gas, the said apparatus further comprising a valve, a push-button valve actuator actuating the valve, the valve including a high pressure obturating means for the propellant cartridge and low pressure obturating means respectively controlling the outlet of the active agent and the admission of air from outside the product container into the product container, the wall of the product container being more permeable to the propellant than the cartridge and the rate of escape of the propellant by permeation through the product container wall being greater than the total rate of escape of propellant from the cartridge into the product container.

This invention relates to dispensing appliances of the aerosol bomb type, permitting the dispensing of a solid or liquid substance in a finely divided state, the said dispensing consisting, in the case of a liquid, of atomization.

This invention is more particularly directed to an appliance of a type known per se which comprises two receptacles placed one within the other, the outer receptacle being a product container containing the product to be dispensed (hereinafter called the active agent) and the inner receptacle being a cartridge containing the propellant, which is usually liquefied gas under pressure.

The dispensing appliance comprises a push-button valve actuator which on the one hand actuates a high pressure obturating means and on the other hand actuates a low pressure obturating means. The low pressure obturating means on the one hand controls the passage of the active agent toward the atomization nozzle situated in the push-button, and on the other hand permits the entry of air into the outer receptacle from outside the receptacle to ensure equality of pressure between the interior of the product container and the atmosphere.

Such dispensers offer a number of advantages as compared to dispensers comprising a single receptacle in which the propellant and active agent are mixed. However a drawback with dispensers of the type having two receptacles is that the propellant tends to pass from the propellant cartridge into the product container, so that the pressure within the latter is gradually increased. It may then expand, the pressure may cause escape of liquid and the propellant gas may possibly dissolve or react with the active liquid, causing a change in the latter.

It is an object of the present invention to obviate the above-mentioned defects.

According to the invention the push-button dispensing appliance, of the aerosol dispenser type, for dispensing a finely divided solid or liquid, comprises an outer receptacle which is a product container of plastic material, containing the active agent to be dispensed and in which is accommodated an inner receptacle which is a propellant cartridge containing a liquefied propellant gas, a valve being controlled by the push-button valve actuator and comprising a high pressure obturating means for the propellant and low pressure obturating means controlling the escape of the active agent and also the admission of air into the product container. The wall of the product container is sufficiently permeable to the propellant so that it permits a rate of escape of the propellant greater than the overall rate of escape of propellant from the propellant cartridge into the product container.

The invention will now be described in connection with the accompanying drawing which is a partial axial sectional view of a dispenser of the aerosol bomb type, and having the wall of the product container permeable to the propellant.

In this dispenser there will be seen at 1 the outer receptacle which is a product container containing the active agent 2 and in which is accommodated a propellant cartridge 3 containing the liquefied propellant 4.

The propellant container 1 is closed by a cap 5 carrying a support 6 having a collar 7 extending therefrom into which the neck of the propellant cartridge 3 fits. There is positioned along the axis of the dispenser a push-button valve actuator 8 containing an atomization nozzle 9 and controlling a high pressure obturating member 11 having a flexible high pressure sealing gasket (not visible) controlling the flow of the propellant towards the nozzle 9, and low pressure obturating means, constituted by a low pressure sealing gasket 12 accommodated between the cap 5 and the support 6. The gasket 12 controls the flow of the liquid from the product container 1 drawn through the dip tube 13 towards the nozzle 9. This gasket also controls the admission of air from outside the product container into the container 1.

In accordance with the present invention the material of the product container 1 is sufficiently permeable to the propellant so that the overall rate of escape of the propellant 4 by permeation through the container wall is definitely greater than the corresponding rate of escape of propellant from the cartridge 3, through the plastic components and through the flexible gasket of the high pressure obturating member 11 and finally escape past the said high pressure obturating member 11.

Thus the overall rate of escape of the product from the cartridge 3 is meant the rate of escape of propellant arising from three factors:

1. Escape by permeation of the propellant through the wall of the cartridge 3 or the inner receptacle.
2. Escape by permeation of the propellant through the constituent members of the high pressure obturator.
3. The high pressure obturator discharge, permitting direct passage of the gaseous propellant from the cartridge into the product container.

In this way the quantity of gas (generally rather small) which escapes from the cartridge 3 into the product container cannot accumulate in the product container, but rather diffuses gradually through the wall of the product container into the atmosphere. The escape from the car-
tridge does not therefore cause any danger of swelling, nor, a fortiori, of bursting the product container, nor any danger of escape of liquid because of overpressure within the product container or again of any reaction of the propellant with the active liquid contained in the said container.

The conditions according to the invention result in the following inequality:

$$F > f_1 + f_2 + f_3$$ (1)

where

- $F$ designates the rate of escape of the propellant permeating through the wall of the product container;
- $f_1$ is the rate of escape of the propellant permeating through the wall of the cartridge;
- $f_2$ is the rate of escape of the propellant permeating through the members of the high pressure obturator and in particular the flexible gasket thereof;
- $f_3$ is the rate of escape past the high pressure obturator.

Use of the inequality (1) makes it possible to determine, for a propellant of a given type, suitable pairs of constituent materials for the walls of the cartridge and product container with the object of avoiding any swelling of the product container.

The rate of flow of the propellant through a wall depends on the nature of the said wall, of its surface, on its thickness and on the temperature. The nature of the material directly affects the coefficient of permeability (or speed of diffusion) of the propellant through the wall.

Thus, the speed of diffusion of hydrocarbons containing fluorine, such as fluoro-trichloroethane, trifluorochloroethane, and so on, through a rigid PVC wall is about 1,000 times faster than the speed of diffusion of simple hydrocarbons (butane, isobutane, propane) through the same rigid PVC wall.

On the other hand the speeds of diffusion of hydrocarbons containing fluorine through polyolefins (polyethylene, polypropylene) are of the same order as the speeds of diffusion of simple hydrocarbons therethrough, but these polyolefins are several hundred times more permeable to simple hydrocarbons (butane, isobutane, propane) than is rigid PVC. The acetal resins are slightly more permeable to simple hydrocarbons than to hydrocarbons containing fluorine.

Similarly, experience shows that a difference in temperature of 30° C. (which may occur due to the storage conditions and the weather during storage) may cause the permeability to vary in a ratio of 1 to 30 and this variation will differ according to the different plastics used.

Experience has shown further that knowing the nature of the propellant and the nature of the wall of the cartridge, it is possible to verify the inequality (1) by a proper choice of the material of the product container, with a safety coefficient sufficiently high for there to be no risk of chance variations which may arise in connection with the term $f_3$ which will reverse the inequality.

If the propellant cartridge is of metal or glass, materials which are completely impermeable to the propellant gas, then $f_1 = 0$. Inequality (1) then becomes:

$$F > f_2 + f_3$$ (2)

Because inequality (2) is much more easily achieved than inequality (1), a wider number of plastic materials can be utilized to form the product container.

In practice the choice of the material for the cartridge will depend on the following factors:

- Cartridges of metal are light and thin and stand up to high pressures, but there is the risk that they will be attacked when the product container contains an active liquid which is corrosive to metal, for instance an aqueous solution containing surface-active agents. Protective lacquers or paints covering the metal prevent corrosion, provided they are not chipped.
- Glass cartridges are not subject to corrosion but they are more fragile and must be thicker.

If the propellant cartridge is made of a plastic material it is subject neither to corrosion nor to fracture and it is lighter. On the other hand the rate of escape of propellant due to the permeability of its wall may be high, and in such a case the plastic material of the wall of the product container must have an even higher permeability.

In selecting the materials of which the receptacles are composed, taking the nature of the propellant into account, use should be made of the following Table I, indicating the classes of permeability as regards two large groups of propellants.

| TABLE I |
|----------------------------------|----------------------------------|
| **Aliphatic hydrocarbon propellants** | **Hydrocarbon propellants containing fluorine** |
| Very high permeability | Rubber and elastomers, Low density polyethylene, Phystated PVC, Cellulose acetate |
| Medium permeability | Polypropylene, Rigid PVC, Acetal resins (Delrin, Hostaform), Collodion acetate |
| Low permeability | Acetal resins (Delrin, Hostaform), Rigid PVC, Cellulose acetate |
| Very low permeability | Polyamides (nylon, Hilan), Polyethylene, Polypropylene, Metal, glass |

Preferably, to obtain a dispenser of the kind defined above, without risk of high pressure building up within the product container, there will be used to form the wall of the cartridge a material which is lower in Table I than the material used for the product container.

In practice the following rules will be found advantageous:

- If it is desired to use as the propellant gas a simple hydrocarbon (butane, isobutane, propane) or a mixture of simple hydrocarbons, the cartridge should be made of a plastic material which is very impermeable to this type of gas, for instance, rigid polyvinyl chloride. For the product container a plastic material which is very permeable to the said gas, for instance a polyolefin (polyethylene or polypropylene) should be used.

The above combination of the two receptacles is suitable when using a simple hydrocarbon as propellant where there is no danger of causing overpressure in the product container containing the active liquid, but it would not be suitable where there was used as propellant a hydrocarbon containing fluorine. In fact, the speeds of diffusion of the hydrocarbons containing fluorine through polyvinyl chloride and the polyolefins are of the same order.

If it is desired to use as propellant a hydrocarbon containing fluorine (F11 propellant, F12 propellant, F2 propellant, F114 propellant and so on) or a mixture of hydrocarbons containing fluorine, there should be used a combination such as a cartridge of acetal resin, and a product container of polyvinyl chloride or polyolefin.

The principal combinations with their properties are summarized in the following Table II.
### SIMPLE HYDROCARBON PROPELLANTS

<table>
<thead>
<tr>
<th>Cartridge materials</th>
<th>Product container materials</th>
<th>Mj</th>
<th>AO</th>
<th>Pn</th>
<th>Ra</th>
<th>PVCp</th>
<th>PVCr</th>
<th>Pn</th>
<th>Pa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene.</td>
<td></td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Polypropylene.</td>
<td></td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Rigid PVC.</td>
<td></td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Plasticized PVC.</td>
<td></td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Acetal resins.</td>
<td></td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Polyamides.</td>
<td></td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Cellulose acetate.</td>
<td></td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Metal with joints.</td>
<td></td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

#### PROPELLANTS CONTAINING FLUORINE

<table>
<thead>
<tr>
<th>Cartridge materials</th>
<th>Product container materials</th>
<th>Mj</th>
<th>AO</th>
<th>Pn</th>
<th>Ra</th>
<th>PVCp</th>
<th>PVCr</th>
<th>Pn</th>
<th>Pa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene.</td>
<td></td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Polypropylene.</td>
<td></td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Rigid PVC.</td>
<td></td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Plasticized PVC.</td>
<td></td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Acetal resins.</td>
<td></td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Polyamides.</td>
<td></td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Cellulose acetate.</td>
<td></td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Metal with joints.</td>
<td></td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

In Table II the symbols have the following meanings:
- Pn = Polyethylene.
- Pp = Polypropylene.
- PVC = Rigid polyvinyl chloride.
- PVCp = Plasticized polyvinyl chloride.
- RA = Acetal resins.
- Pa = Polyamides.

There will preferably be used therefore, according to the invention, the combinations which produce condition 0 and, if the pressure conditions are not too severe, those marked +. The combinations marked ± are not within the scope of the invention.

By way of example, the cartridge 3 and its attachments, when filled with propane, allow between 2 and 10 mg. per day of propellant to escape. If they are placed in a 250 ml. product container 1, of rigid PVC 0.6 mm. thick, this receptacle can only allow escape by permeation through the wall thereof 2 to 3 mg. of propane per day. The pressure within product container 1 will thus be built up. On the other hand, if the same product container is made of high density polyethylene, it will pass several grams of propane per day, and there will be no risk of swelling. Then again, if the cartridge 3 is filled with trifluoro-trichloromethane, the permeability will be from 1 to 6 mg. per day and it could be placed either in a product container of rigid PVC or in a polyethylene product container either of which could allow escape of a quantity on the order of 1 gram of trifluoro-trichloromethane per day.

Further details of certain quantitative data will be given, based on the following assumptions:

1. A cartridge of aluminium, i.e. f1=0.
2. A product container of polyvinyl chloride.
3. The rate of escape f2 of propellant gas through the pressure obturator essentially depends on the porosity of the flexible gasket with respect to the propellant and the relative pressure P of this propellant.
4. With propane, P at 20°C is approximately equal to 9 kg. per sq. cm., and f2 lies between 2 and 10 mg. per day.
5. With the F12 propellant, P at 20°C is equal to 4.7 kg. per sq. cm. and f2 lies between 1 and 5 mg. per day.
6. The rate of escape f2 depends on the relative pressure of the propellant and generally lies between 0 and 1 mg. per day.
7. For the product container 1, at a given temperature, we have Fp = Kp.e where K is a coefficient, p the speed of diffusion of the propellant through PVC, S the surface area of the container and e its wall thickness. With a product container of a quarter of a litre capacity, having a surface of about 300 sq. cm. and a thickness of 0.6 mm., there is found:
8. Fp = 3 mg. per day.
9. Fp = 1,000 mg. per day for propellant F12.
10. Under these conditions, with a cartridge 3 of aluminium, a product container 1 of PVC, and propane, we have:
11. Fp = 3 mg. per day.
12. As the inequality (2) is not maintained, there will be swelling.

On the contrary, with the propellant F12:
13. Fp = 1,000 mg. per day.
14. f1=0; f2=3.5; f3=1, or a total of 4.5.
15. The difference between these two values is such that swelling is fundamentally impossible.
16. The selection table given above was prepared from calculations of this kind.
17. It will be noted that in the invention mechanical escapes and escapes due to permeation through the low pressure obturator member of the product container are not taken into account. In fact such escape always acts favorably in preventing swelling. This is in fact one of the advantages of the invention, that it should offer a simple condition of the nature of inequality (1) or (2).
18. Of course the invention is not restricted to a particular mechanical structure of the dispenser and applies to any of the variants that may be made of the type represented.
19. What I claim is:
20. 1. A push-button dispensing apparatus, of the aerosol bomb type, for dispensing solid or liquid material in a finely-divided state, and comprising a product container containing the active agent to be distributed, a propellant cartridge within said product container and containing a liquefied propellant gas, the said apparatus further comprising a valve, a push-button valve actuator actuating the valve, the valve including a high pressure obturation means for the propellant cartridge and low pressure obturation means respectively controlling the outlet of the active agent and the admission of air from outside the product container into the product container, the wall of the product container being more permeable to the propellant than the cartridge and the rate of escape of the propellant by permeation through the product container wall being greater than the total rate of escape of propellant from the cartridge into the product container.
21. 2. An apparatus as claimed in claim 1 in which the total rate of escape of propellant from the inner receptacle corresponds to the sum of the rates of escape by permeation of the propellant through the wall of the cartridge, permeation of the propellant through the members constituting the high pressure obturation means and of the mechanical escape of propellant through the high pressure obturation means.
22. 3. An apparatus as claimed in claim 1 in which the propellant is a simple hydrocarbon, and the cartridge is rigid polyvinyl chloride and the outer receptacle is polyolefin.
4. An apparatus as claimed in claim 1 in which the propellant is a simple hydrocarbon, and the cartridge is polyamide and the outer receptacle is polyolefin.

5. An apparatus as claimed in claim 1 in which the propellant is a hydrocarbon containing fluorine, the cartridge is acetal resin and the product container is polyvinyl chloride.

6. An apparatus as claimed in claim 1 in which the propellant is a hydrocarbon containing fluorine, the cartridge is acetal resin and the product container is polyolefin.

References Cited

UNITED STATES PATENTS

2,888,208 5/1959 Fedt -------------- 239—308
3,245,435 4/1966 Healy -------------- 222—399 X
3,326,469 6/1967 Abplanalp et al. ----- 239—308

ROBERT B. REEVES, Primary Examiner.
HADD S. LANE, Assistant Examiner.

U.S. Cl. X.R.