PROCESS FOR STERILIZING AND FILLING AEROSOL CONTAINERS

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Filed: Sept. 10, 1971

Appl. No.: 179,533

Related U.S. Application Data
Continuation-in-part of Ser. No. 878,879, Nov. 21, 1969, abandoned.

U.S. Cl. ................................................. 141/3
Int. Cl. .............................................. B65b 3/04
Field of Search ................................. 141/3, 20, 48, 91, 141/92; 21/58, 108, 109, 28, DIG. 4; 99/182, 189, 214; 134/35, 37; 29/DIG. 7; 128/218 S

ABSTRACT
The invention provides a process for sterilizing and filling of aerosol containers with sprayable or foamy products which briefly comprises providing a sealed and valved-empty aerosol container, sterilizing the sealed aerosol container, filling the sealed sterile aerosol container first with a propellant gas, and, thereafter, filling the sealed sterile propellant-containing aerosol container with the sprayable or foamy product.

29 Claims, No Drawings
PROCESS FOR STERILIZING AND FILLING AEROSOL CONTAINERS

This application is a continuation-in-part of U.S. Pat. Ser. No. 878,879, filed Nov. 21, 1969 (now abandoned).

SUMMARY OF THE INVENTION

The invention relates to a process for the sterile packaging of sprayable or foambale products, particularly of sterilized, inherently easily perishable foodstuffs or of sterile, medicinal preparations in aerosol containers, which are sterilized before filling.

Aerosol containers have found use to a considerable extent as packaging for cosmetic products as well as for pest control agents, paints, cleaning agents and similar products, since with their help the user can produce a spray mist or a foam simply and in a precise dosage. Attempts to package either easily perishable foodstuffs or sterile pharmaceutical preparations in aerosol containers and to put them on the market in this form have for long failed because no one has succeeded in sterilizing the containers and valves sufficiently and in preventing the entry of fresh germs on filling.

It has been attempted to sterilize the open container thoroughly and thereafter to fill it in the usual way while maintaining scrupulously sterile conditions, the material to be filled being introduced after sterilization and the valve then put on and finally the propellant gas forced in. It has however been found that this procedure does not work satisfactorily; for example, the safe storage period for ultrahigh-heated cream, which with sterile packaging can normally be kept in a closed container for at least four weeks, amounted to only a few days. Such a result is of little use, since the packaging of foodstuffs in aerosol containers is too expensive for such a short period of safe storage and is not to be considered at all in relation to pharmaceutical products on account of the strict sterility requirements.

The subject of the invention is nevertheless a process for the sterile packaging of sprayable or foambale products in aerosol containers; the process is characterized in that first the valve is put on the empty aerosol container and then the container sterilized and that thereafter the propellant gas and then the sprayable or foambale products are filled through the valve. By means of this process which represents a departure from the usual packaging process a really thoroughly sterile filling of aerosol containers is achieved for the first time. By sterilization of the empty container with the valve in place it is guaranteed that all germs within the container and the valve are destroyed; the material to be filled does not come into contact later with any non-sterile parts provided that, in accordance with the invention, one brings not only the propellant gas but also the actual material to be filled through the valve into the sterile aerosol container already provided with valve. Practical tests have proved that the safe storage period of foodstuffs packaged according to this invention correspond completely to those which are obtained with germ-free packaging of sterilized products in simple packaging containers. It has been found to be essential to fill the aerosol containers first with the propellant gas and then with the product, since the emulsion-type materials, e.g. milk or cream, will be destroyed and will separate into their components if the product is introduced into the evacu-ated container and hits the walls thereof with the pressure prevailing in the filling head.

BRIEF DESCRIPTION OF THE INVENTION

According to an embodiment of the invention here produced so that one fills the empty aerosol containers through the valve, after putting this on, with gaseous or vaporized sterilizing agent, removes the sterilizing agent after a time sufficient for substantially complete destruction of all the germs, and then fills the aerosol container through the valve with the propellant gas and the sprayable or foambale products.

The sterilizing agent used in accordance with the invention should preferably be gaseous at room temperature, that is at about 20° to 25° C, or at least possess so low a boiling point that it can be pumped off quickly even at a moderate vacuum. A particularly preferred sterilizing agent is ethylene oxide, the boiling point of which lies at +12.5°C and which shows outstanding germicidal activity even at relatively low concentration. For sterilization of the containers one preferably proceeds in such a way that the aerosol containers after putting on the valves are first evacuated to the greatest possible extent and then filled with the sterilizing agent, the quantity of which depends on the activity, the duration of effect as well as possibly (when using superatmospheric pressure) on the internal pressure allowable for the aerosol container. When using ethylene oxide as sterilizing agent, a pressure of about 0.25 to 1.0 atm. has been shown to be completely satisfactory, if the containers filled with ethylene oxide are then left to stand for several hours, preferably about 24 hours or even longer.

For complete removal of the sterilizing agent from the sealed aerosol containers these are flushed repeatedly with an inert gas, such as nitrogen or carbon dioxide. For a complete removal of the gaseous or vaporized sterilizing agent it suffices to evacuate the containers repeatedly (e.g. three times) and to force in an inert gas after each evacuation. Consequently the inert gas pressure employed depends substantially only on the resistance to pressure of the containers; in the usual aerosol containers with an allowable loading capacity (a test pressure) of 18 atm. and a normal filling pressure between 6 and 8 atm., an inert gas pressure between 5 and 10 atm. can advantageously be used. The higher the inert gas pressure, the more the sterilizing agent is diluted. After flushing three times with inert gas in the manner described, it is later no longer possible to detect analytically any traces of the sterilizing agent in the product.

For reducing the consumption of sterilizing agent as well as for avoiding any danger to the operatives and of contamination of the atmosphere, it is preferred to recover the sterilizing agent after pumping it off from the aerosol containers and, if desired, to re-use it. This can take place in the usual way, for example by insertion of a cooling trap cooled to a suitable temperature in the off-gas line.

After the thorough flushing with inert gas the filling of the aerosol containers according to the invention takes place. It is an essential feature of the invention that the actual material to be filled, that is the products to be released as spray mist or as foam, are filled after putting on the valve and sterilization of the container through the valve. This operation takes place after the filling of the propellant gas. As propellant gas the usual...
compounds, particularly halogenated hydrocarbon compounds can be used. For foodstuffs, nitrous oxide (laughing gas) is particularly suitable on account of its neutral taste and its relative physiological inoffensiveness, but, if desired, a mixture of nitrous oxide and carbon dioxide can be used. Optionally an inert gas such as nitrogen may be used to dilute the propellant gas; since the propellant gases dissolve well in most substances, laughing gas particularly in water-containing products, the filling of the propellant gas into the empty container has the additional advantage that the full quantity of propellant gas can be regulated very exactly by simple pressure control which is not possible to the same extent with a reversed sequence of operations, since the solubility of the propellant gas varies strongly dependent respectively on the prevailing temperature and the solution properties of the mixture of products.

The proportion of propellant gas to filling material can therefore be kept particularly constant in accordance with the procedure of this invention. It is self-evident that in this case the filling pressure for the material to be filled must be so high that the propellant gas pressure prevailing in the can is quickly overcome, yet the excess pressure needed is comparatively small, so that the product to be filled is subjected only to mild physical forces.

According to a further embodiment of the invention, one carries out the process in such a way that one sterilizes the aerosol container after putting on the valve by short heating at a raised temperature, cools under sterile conditions and fills or even fills hot and then cools.

Preferably for sterilization it is heated for about 5 minutes at about 140°C. If water is present in the container its interior then will be sterilized by superheated steam. Alternatively, superheated steam may be supplied to the container. Heating can for example take place by immersing the container in a hot fluid bath or by introducing the container into a hot gas atmosphere, e.g. in a hot-air oven. During this the container can be filled with air or preferably be evacuated. According to another preferred embodiment the aerosol container is filled before heating with carbon dioxide or with a sterilizing agent. In this case the sterilizing agent should be gaseous or vaporized at the sterilization temperature, that means that one can use both sterilizing agents which are already gaseous under normal pressure at room temperature, such as e.g. ethylene oxide, and sterilizing agents which have a higher boiling point but which are transformed into the vapour state at the sterilization temperature of 140°C, e.g. ethanol.

According to a particularly preferred modification of the latter embodiment of the process according to the invention, the aerosol containers are filled with the propellant gas before sterilization at a raised temperature. Experimental observations have shown that the propellant gases used normally, namely laughing gas (N₂O) or halogenated hydrocarbons, themselves display a certain germicidal effect which can be increased still further by heating to higher temperatures. If desired, additional sterilizing agents, e.g. ethanol, can be added to the propellant, provided their presence in the end product is not troublesome.

With the above procedure it is easily possible to fill the aerosol containers with the necessary total quantity of propellant gas so that the normal filling pressure of about 6 to 8 atm. is obtained, for with an increase of temperature from about 20°C to about 140°C the pressure only increases by a factor of about 1.4 and therefore attains a maximum of only about 12 atm., so that aerosol cans with a test pressure of about 18 atm. are usable. According to this procedure, an aerosol container filled with propellant gas is thus obtained, whose inner space including the valve is completely sterile. The process is terminated by filling the sterile product likewise through the valve into the aerosol container.

For cooling, the heated aerosol containers are preferably fed through a sterile fluid bath and then dried by blowing with a sterile gas, preferably hot air. Cooling can take place immediately after sterilization before filling the material to be filled or however only as the last step, after the aerosol container has been filled in the hot state.

The process according to the invention is suitable for the packaging of all products which, by reason of their easy perishability, possess a long period of safe storage only after thorough sterilization, in particular of foodstuffs such as milk products. Thus for example so-called sterile cream (heated in autoclaves for about 30 minutes at 120°C) or preferably H-cream (flash-heated for about 3 seconds at 150°C) can be packaged according to the invention; therefore, instant-ready whipped cream is available to the user at any time in a particularly convenient form even in the smallest quantities, while the period of safe storage of the product corresponds to that of the normally packaged sterilized cream and therefore amounts to four or more weeks.

The foamed ("whipped") cream withdrawn from an aerosol container is particularly light and therefore may surpass normal whipped cream in volume quite considerably. On release from an aerosol container the cream turning into whipped cream increases in volume 6 to 8 times so that 0.25 litres of cream yield up to 2 litres of whipped cream.

Other sterilized products which can advantageously be packaged according to the invention are for example butter-creams for the production of tarts, herbal butter, which is obtained in a particularly light and foamy form, cheese spread for decorating dishes and other foamy products.

Easily perishable cooking fats, icings or toppings, can likewise be packaged as sprayable products. A further possibility of use for the invention lies in the region of packaging sterile medicinal or medicated cosmetic preparations, e.g. of liquid plasters, sun protecting agents, treatment agents for burns and sunburn and others.

A particularly rational procedure results if one carries out the packaging process according to the invention continuously directly in conjunction with the sterilization plant for the product to be packaged. The process therefore takes the place of the usual process for packaging products in normal packaging containers.

EXAMPLE 1

Conventional aerosol cans with a lining which is not attacked by ethylene oxide (so-called gold varnishing), with about 510 ml. capacity, were sealed with a suitable valve. Then the can was evacuated to a pressure of about 20 mm Hg and filled with 1 g. of gaseous ethylene oxide so that the pressure in the can amounted to about 0.5 atm. After standing for 24 hours, the ethylene oxide was withdrawn from the can and replaced by carbon dioxide, the gas pressure amounting to about 8
atm. Evacuating and filling with inert gas was repeated twice and into the re-evacuated can nitrous oxide was introduced until an internal pressure of 8 atm. had been attained. The 260 g. flash-heated cream (co-called H-
cream) were filled through the valve. Then the can was rolled through a water bath to test for gas-tightness. During rolling a thorough mixture of the can contents took place which led to the fact that a part of the propellant gas is dissolved and the internal pressure drops to about 6 atm.

On actuation of the valve a particularly light whipped cream is obtained. The quantity of cream filled yielded about 2 litres of whipped cream. After standing for four weeks the cream was unchanged, while an H-cream filled in a sterilized aerosol container in accordance with the conventional packaging process had already gone sour after four days. No traces of ethylene oxide could be detected in the whipped cream on analysis by gas chromatography. Before filling, the cream can be mixed with usual cream stiffening agents, e.g. one of the commercially available starch-based agents, an emulsifier, such as monoglyceride and, if desired, with a stabilizer, e.g. an alginate. If desired, flavouring substances, sugar or even colouring substances can be added in addition so that it is possible to produce a whipped cream of a particular flavour and/or colour.

EXAMPLE

The process of Example 1 was repeated on a fully-automated filling station. From a total number of 120,000 aerosol containers filled in this manner, every thirty minutes one can was withdrawn for quality control. Altogether, 320 samples were taken from the production line. The test containers were first incubated for seven days at 37°C in order to allow possibly present micro-organisms to develop. Following this treatment, a bacteriological evaluation was carried out. All 320 samples contained bacteria proved to be bacteriologically sterile, i.e., the total bacteria number on Chinese-blue lactose agar was zero bacteria per gram. The test for coli bacteria was also negative in all instances.

The samples were also investigated organoleptically. This test also did not give rise to any complaints relative to the large number of samples which had been withdrawn at random.

After standing at ambient temperatures for several months, the cream content of the aerosol containers did not show any deterioration. This also proves that the process of this invention makes it possible for the first time to fill aerosol containers with cream under completely sterile conditions.

EXAMPLE 3

The process of Example 1 was repeated, but the cream was replaced by a burn ointment composition made up of the following ingredients:

- Benzotrieniumchloride: 0.1 g
- Cetylpyridiniumchloride: 0.01 g
- Polymethylene glycolmonodecyIether: 2.08 g
- Urea pura: 7.00 g
- Special gel: 40.00 g

260 g. of this composition were introduced into each valved-empty sterile aerosol container, after filling with halogenated hydrocarbons as propellant gas. Due to the particularly mild filling conditions, the sensitive gel was not destroyed during the filling step. The contents of the aerosol containers proved to remain sterile on standing for several months at ambient temperatures.

We claim:

1. A process for the sterile packaging of sprayable or foamy products in aerosol containers, which process comprises:
   a. providing a sealed and valved-empty aerosol container;
   b. sterilizing the sealed aerosol container;
   c. filling the sealed sterile aerosol container first with a propellant gas, and, thereafter, d. filling the sealed sterile propellant-containing aerosol container with the sprayable or foamy product.

2. A process for the sterile packaging of sprayable or foamy products in aerosol containers, which process comprises:
   a. providing a sealed and valved-empty aerosol container;
   b. introducing a gaseous or vaporized sterilizing agent through the valve into the container;
   c. removing the sterilizing agent from the sealed sterilized aerosol container after a period of time sufficient for sterilization of the interior of the container;
   d. filling the sealed sterile aerosol container first with a propellant gas, and, thereafter, e. filling the sealed sterile propellant-containing aerosol container with the sprayable or foamy product.

3. The process of claim 2 which includes: flushing the sterilized aerosol container with an inert gas after removal of the sterilizing agent.

4. The process of claim 2 which includes: removing the sterilizing agent from the interior of the sterilized aerosol container by withdrawing the sterilizing agent from the container through the valve, and flushing the evacuated sterile aerosol container with an inert gas several times in succession to remove any residual sterilizing agent.

5. The process of claim 2 which includes: retaining the sterilizing agent within the aerosol container for at least several hours prior to removing the sterilizing agent.

6. The process of claim 2 wherein the sterilizing agent includes ethylene oxide.

7. The process of claim 2 which includes: evacuating the sterilizing agent from the sterile aerosol container and filling the evacuated sterile aerosol container with inert gas, the evacuating and filling steps carried out several times in succession and at increased pressures.

8. The process of claim 2 which includes: recovering the sterilizing agent removed from the sterile aerosol container and recycling all or a part of said sterilizing agent for use in sterilizing other aerosol containers.

9. The process of claim 2 which includes evacuating the sealed aerosol container, and, thereafter, sterilizing the container by injecting superheated steam through the valve into the interior of the sealed evacuated aerosol container.

10. The process of claim 2 wherein the propellant gas is selected from the group comprising nitrous oxide, carbon dioxide or a mixture of nitrous oxide and carbon dioxide.

11. The process of claim 2 which includes employing as the foamable or sprayable substance a cream product.
12. A process for the sterile packaging of a cream-like product in an aerosol container, which process comprises:
   a. providing a sealed and valved-empty aerosol container;
   b. introducing a gaseous or vaporizable sterilizing agent through the valve into the sealed aerosol container;
   c. evacuating the sterilizing agent through the valve from the interior of the aerosol container after a period of time sufficient for the sterilizing agent to sterilize the interior of the aerosol container and the valve;
   d. flushing the evacuated sterile aerosol container through the valve successively with an inert gas;
   e. filling through the valve the sterile evacuated flushed aerosol container with a propellant gas; and, thereafter,
   f. filling the sterile aerosol container through the valve with a cream product.

13. The process of claim 12 wherein the sterilizing agent is ethylene oxide.

14. The process of claim 12 wherein the sterilizing agent is retained within the interior of the sealed aerosol container for about 24 hours or longer.

15. The process of claim 12 wherein the propellant gas comprises nitrous oxide, carbon dioxide, or a mixture thereof and the product is a sterile cream product or H-cream product.

16. A process for the sterile packaging of sprayable or foamy products in aerosol containers, which process comprises:
   a. providing a sealed and valved-empty aerosol container;
   b. heating the empty sealed aerosol container at an elevated temperature to sterilize the interior of the aerosol container;
   c. filling the sealed sterile aerosol container first with a propellant gas; and, thereafter,
   d. filling the sealed sterile propellant-containing aerosol container with the sprayable or foamy product.

17. The process of claim 16 wherein the propellant comprises nitrous oxide, carbon dioxide, or a mixture thereof.

18. The process of claim 16 which includes prior to heating evacuating the sealed valved-empty aerosol container and injecting superheated steam through the valve into the interior of the sealed evacuated aerosol container.

19. The process of claim 16 which includes cooling the heated empty aerosol container under sterile conditions before filling the sterilized container.

20. The process of claim 16 which includes heating the sterile aerosol container for about 5 minutes at about 140° C.

21. The process of claim 16 which includes filling the sealed aerosol container before heating with a carbon dioxide propellant, and, thereafter, heating the carbon dioxide-containing sealed aerosol container.

22. The process of claim 16 which includes before heating filling the sealed aerosol container through the valve with a sterilizing agent, and subsequently removing the sterilizing agent.

23. The process of claim 16 which includes before heating filling the sealed aerosol container through the valve with a propellant gas and a sterilizing agent.

24. The process of claim 16 which includes cooling the sealed heated aerosol container by immersing in a sterile bath and drying the container by blowing with a sterile gas.

25. The process of claim 16 wherein the product is a sterile cream product of an H-cream product.

26. The process of claim 1 which includes employing as the foamable or sprayable substance a cream product.

27. The process of claim 1 wherein the propellant gas is selected from the group comprising nitrous oxide, carbon dioxide or a mixture of nitrous oxide and carbon dioxide.

28. The process of claim 1 which includes evacuating the sealed aerosol container, and, thereafter, sterilizing the container by injecting superheated steam through the valve into the interior of the sealed evacuated aerosol container.

29. The process of claim 1 which includes sterilizing the sealed aerosol container by introducing a gaseous sterilizing agent into the container through the valve; removing the sterilizing agent; and flushing the sterile valved container after removal of the sterilizing agent with an inert gas prior to filling the sealed sterile aerosol container.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,763,900 Dated October 9, 1973

Inventor(s) Hubertus Graf Zu Solms-Baruth and Egon Honisch

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In the headnote, after item "[63]" and before item "[52]", insert the following paragraph:

--Foreign Application Priority Data

Nov. 26, 1968 Switzerland.................17558/68
Jan. 3, 1969 Germany....................P 19 00 231.4
Aug. 19, 1969 Germany....................P 19 42 056.5
Oct. 4, 1969 Germany....................P 19 50 165.6

Signed and sealed this 12th day of February 1974.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR. C. MARSHALL DANN
Attesting Officer Commissioner of Patents