

Jan. 14, 1964

M. B. EPSTEIN

3,117,699

PRESSURE DISPENSER WITH PROPELLANT DEVELOPED IN SITU

Filed April 14, 1961

2 Sheets-Sheet 1

Fig. 1

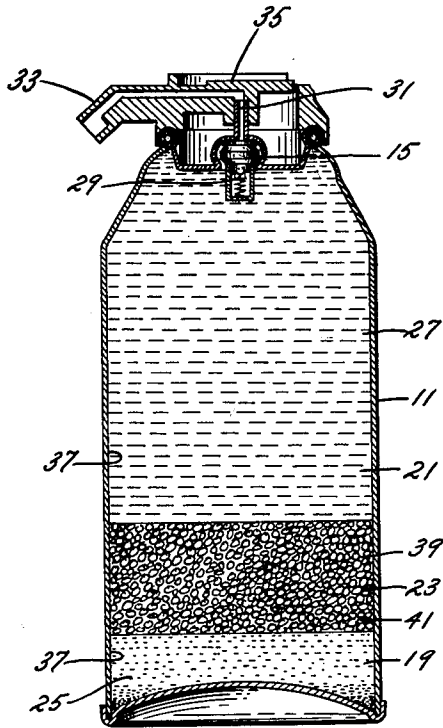
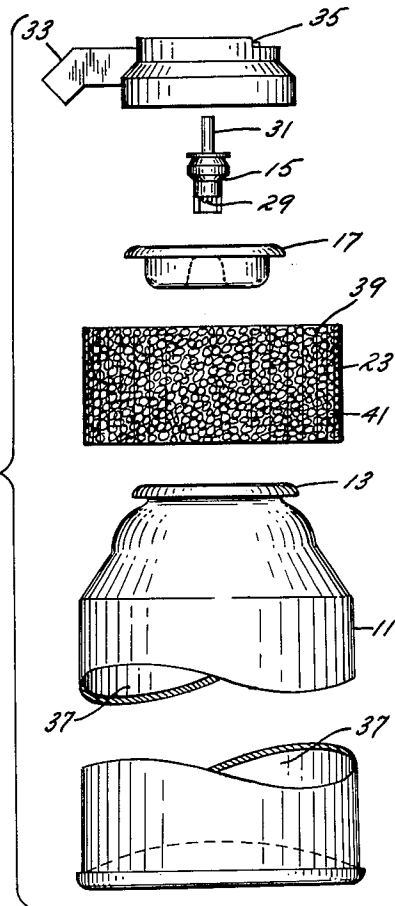


Fig. 2



INVENTOR.
MORTON BATLAN EPSTEIN
BY *Phonae M. Hammond*
Attorney

Jan. 14, 1964

M. B. EPSTEIN

3,117,699

PRESSURE DISPENSER WITH PROPELLANT DEVELOPED IN SITU

Filed April 14, 1961

2 Sheets-Sheet 2

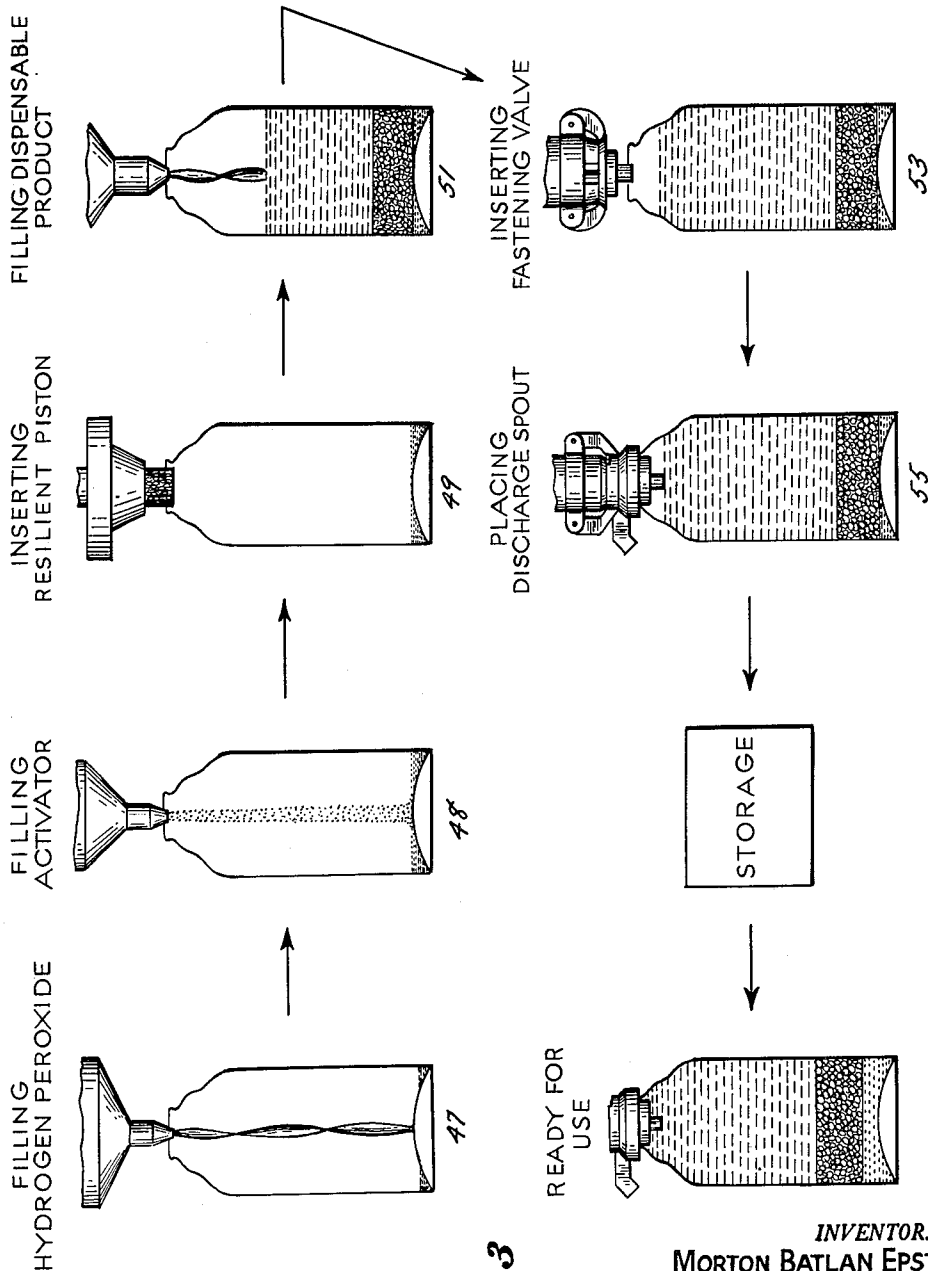


Fig. 3

INVENTOR.
MORTON BATLAN EPSTEIN
BY *Thomas M. Hammond*
Attorney

1

3,117,699

PRESSURE DISPENSER WITH PROPELLANT DEVELOPED IN SITU

Morton Batlan Epstein, Linden, N.J., assignor to Colgate-Palmolive Company, New York, N.Y., a corporation of Delaware

Filed Apr. 14, 1961, Ser. No. 103,165
7 Claims. (Cl. 222-389)

This invention relates to pressure systems. More particularly the invention relates to gas generating systems for pressurizing a container such as an aerosol type dispenser from which a fluent material is dispensed and to a method for manufacturing such a pressurized dispensing system.

The invention will be readily understood from the following description and the attached drawings in which:

FIGURE 1 is an axial vertical elevation of a preferred dispensing container of fluent material wherein propellant material is releasing pressurizing gas;

FIGURE 2 is a view of the disassembled elements of such a container; and

FIGURE 3 is a schematic representation of a method of manufacturing pressurized dispensers in accordance with this invention.

Many types of aerosol systems are known. However, many of the known systems present serious drawbacks in that the propellants employed are usually added to the container as a gas through the dispensing valve after the container has been sealed. On the other hand, prior to the development of commercial methods of pressure filling, liquefied gaseous propellants were refrigerated and added to the cooled container before the dispensing valve and container were put into place. After sealing of the container, heating of the liquefied gas caused development of dispensing pressure. This cold-fill method led to loss of propellant due to vaporization during filling and furthermore was restricted to the use of those products which were not harmed by the low temperatures necessary. Accordingly, elaborate equipment and careful procedures were necessary in order to obtain an aerosol system having suitable dispensing pressure. In such systems the propellant gas is usually added to the container last, since the contents to be dispensed can be conveniently added at atmospheric pressure through a relatively large filling opening before the container is sealed. Consequently, the filling machinery required is less intricate and more economical. On the other hand, addition of propellant through the discharge valve is usually slow in operation in comparison with the speed of the automatic machinery employed for filling the container with the non-pressurized contents. It is highly desirable, therefore, to have a propellant or propellant generating material which can be added to the container with the same ease and speed as the non-pressurized contents and at atmospheric pressure.

A propellant generating material that can be added to the container at atmospheric pressure must be one that meets certain requirements. For example, such a propellant generating system must be relatively stable at atmospheric pressures and normal room temperature but one which will release gas in a sufficient amount to build up the required dispensing pressure in situ in the container. Furthermore, in such a propellant generating system the gas released should be one which does not adversely affect the product to be dispensed or adversely affect the area or surface to which the dispensed product is applied. In addition, the propellant generating system should be one from which the release of gas takes place relatively slowly or one from which the release of gas can be controlled, that is one from which the release of gas can be speeded up by catalysis or activation. A fur-

2

ther requirement is that the product remaining after release of gas be one that is not harmful to the product to be dispensed. Furthermore, the propellant generating system before or after the release of gas should be one that does not affect the container either by corrosion, or in some other manner.

It has now been found that hydrogen peroxide meets the above requirements for an in situ gas generating system when employed in pressurized dispensing containers. The hydrogen peroxide releases oxygen and forms water, generally harmless and usually already present in the dispenser.

Although hydrogen peroxide of widely varying strength can be employed, relatively strong hydrogen peroxide is generally more effective. Concentrations as low as 20% hydrogen peroxide can be employed as a source of oxygen. On the other hand, it is preferred to use at least 70% hydrogen peroxide. When stronger concentrations are employed, the amount necessary to generate a required volume of gas is smaller and less water will be present in the system after oxygen is released. The amount of hydrogen peroxide of a given concentration necessary to provide the required amount of oxygen needed to give a particular dispensing pressure can be readily calculated. The amount of oxygen needed to build up the necessary pressure in a particular container will depend upon a number of factors among which are the size of the container and the amount of product to be dispensed therefrom. Accordingly, enough hydrogen peroxide is employed to release sufficient oxygen to build up the required dispensing pressure in the dispensing container to expel substantially all the product therefrom.

Although commercially available hydrogen peroxide generally contains a stabilizer it will release oxygen over a relatively long period of time, and thus gradually build up to full calculated pressure, but it is preferred to employ a catalytic activator to speed up and control the release of the gas. Any known catalytic activator which causes decomposition of hydrogen peroxide can be utilized in the practice of this invention. For example, heavy metal cations or enzymes which catalyze the release of oxygen from hydrogen peroxide can be used to effect controlled release of oxygen. Among such compounds are copper or iron salts such as copper sulfate, ferrous sulfate, ferrous ammonium sulfate, and other heavy metal cations in salt form. Among the enzymes there are catalase and other suitable enzymes or sources of these enzymes, such as blood. In addition, bases can be utilized to raise the pH of the hydrogen peroxide solution to a value at which release of gas is accelerated. Normally, the amount of catalytic activator present in the system will be relatively small in comparison with the amount of hydrogen peroxide employed. Amounts ranging from about 0.05% to about 0.5% by weight, based on the weight of hydrogen peroxide, of catalytic activator are suitable for effecting controlled and substantially complete release of oxygen gas from the hydrogen peroxide. However, this range is not critical and greater or lesser amounts can be employed if desired.

The oxygen generating system of this invention can be used with any type and design of container normally suitable in the manufacture of pressurized products. The container can be made of metal such as iron, aluminum, etc., glass, plastic and combinations of these materials or any materials which are capable of withstanding the pressure built up therein. However, for the sake of simplicity, the present invention is disclosed herein as it is employed with a container having the particular structure set forth in detail hereinbelow.

Referring now to FIGURE 1, there is shown a preferred type of dispensing container designated by numeral 11. The container has a top opening defined by a

rim 13 adapted to have a dispensing valve 15 directly staked to the container or which may be fastened to a valve fitment 17 which, in turn, is staked and rolled into pressure tight engagement with container 11 at rim 13. Gasket between the container, valve and fitment assure pressure tight joints. Dispensing valve 15 and container 11, as well as any sealed joints or seams therein, must be capable of withstanding, without leaking, a dispensing pressure, which is often about 40 pounds per square inch but in some instances may be from about 20-200 pounds per square inch.

Inside the container and separating its interior into a propellant section 19 and dispensing or product section 21 is a floating resilient piston 23 of non-communicating cellular structure, of cell diameters within the range between about 0.01 and 0.2 inch and of wall thickness between 0.001 and 0.005 inch. The cellular piston is made of a foam of a synthetic organic resinous material, such as polystyrene, polyethylene, polyurethane or other foamable, preferably resilient, plastic. In propellant section 19 is a pressurized oxygen gas 25 which acts to move the piston upward forcing fluid product 27 through openings 29, valve stem 31 and out spout 33 when valve button 35 is manually depressed to open position. Piston 23 presses tightly against the interior side walls 37 of container 11 to maintain the separation of propellant and product sections. Walls 39 of cells 41 of the piston 23, in the embodiment illustrated, are permeable to the propellant gas to allow gradual entry of gas at higher pressure through the cells which are initially at about atmospheric pressure. This permeability prevents collapse of closed cell foam pistons due to development of dispensing pressures in the container.

In FIGURE 3 there are schematically illustrated the processing operations for manufacturing a pressurized product according to the preferred form of this invention. Numeral 47 is a highly accurate gravimetric filling machine which adds a precise small quantity of hydrogen peroxide to the container. With the hydrogen peroxide there may be included a pre-blended proportion of activating material which causes the release of oxygen gas from the hydrogen peroxide. In the absence of preblending an additional small quantity of catalytic activator may be added before, with or after the hydrogen peroxide, as at filler 48, or may be otherwise placed in the propellant section of the container with it. The amounts of hydrogen peroxide and activator employed, as mentioned hereinabove, will be such as to cause the release of sufficient pressurizing oxygen gas to satisfactorily discharge fluid product contents at desired working pressures and the activator will be sufficient to release all available oxygen from the hydrogen peroxide. After the addition of the oxygen generating substances, the container is then advanced to an inserting machine 49 which places the resilient cellular piston into the can through the top opening thereof. In the embodiment illustrated, it will be noted that the piston must be partially distorted to allow insertion through the restricted top opening in the container. Filling machine 51 automatically adds the required quantity of dispensable fluid product atop the piston. Because the piston presses tightly against the side walls of the container and because the cells, though permeable to gas, do not allow the passage of liquid or pasty substances, none of the product charged reaches the propellant section.

Still at atmospheric pressure, as in the preceding operations, an assembly of valve and valve fitment is automatically inserted, stacked and rolled in place by a conventional machinery 53 for this purpose. Subsequently, a spout member is installed by machinery 55. From this point, the handling and packing operations proceed as with other products, with a single exception. The heat testing of filled containers is omitted, because it would usually cause a premature release of oxygen gas. Such heat testing may be conducted, if desired, after the dis-

pensing container has been stored for a sufficiently great length of time without actuation of the discharge valve to develop all the propellant pressure for which it was designed.

During the storage period the generation of oxygen continues until all the hydrogen peroxide has released its gas content. The pre-measured amount of hydrogen peroxide, computed to be that necessary to raise the dispensing container to correct pressure, is preferably completely consumed. This gives most accurate dispensing pressure control. The period in which propellant is developed may be as short as several hours or as long as three months. The development of full pressure in a few hours can be effected without premature release of gas during the filling operation by utilizing slow starting compositions. These may be mixtures in which the catalytic activator is not initially in intimate contact with the hydrogen peroxide or may be those where the products of reaction have an accelerating effect on oxygen release. In the former case, either catalytic activator or hydrogen peroxide may be encapsulated by coating with an insulating material which is slowly dissolved or otherwise penetrated by a reactant. Suitable encapsulating materials are gelatin, polyvinyl alcohol, methylcellulose and the natural gums. Comparatively quick release of oxygen is sometimes advantageous because it permits a minimum of hold up of filled containers awaiting testing before they can be shipped. However, where the hydrogen peroxide and activator are very accurately measured into the containers with the precision equipment presently available it is expected that special pressure testing of all filled cans will not be required. Even if it should be necessary to test every filled package, other testing methods, such as those which are based on electronic means and are suitable for checking an entire packed case, may be used to assure that no off pressure product is released to market.

Normal warehousing of filled product may continue for as long as three months and therefore the required holding time for the slower developed propellants is not a significant disadvantage of the production method. On the contrary, the gradual release of oxygen and slow increase of internal pressure in the container are decidedly useful, even necessary for the manufacture of certain types of floating piston aerosol dispensers. Those pistons made of what are commonly termed closed cell foams, i.e., those in which the globular cells are non-communicating, are usually foamed at atmospheric pressure and therefore the gas pressure in the cell interior is lower than the desired dispensing pressure. When such a piston is inserted in a dispenser and the dispenser is subsequently pressurized, the external pressure, which may be from about 20-200 pounds per square inch, even higher in some special cases, will cause the collapse of resilient pistons or of any foam in which the cell wall itself cannot withstand the high pressure differential that is imposed upon it. If the piston is resilient or elastic and permeable to gas penetration, the pressures will become equalized and it will return to enlarged form. However, the initial collapse upon pressurizing will create passageways between the propellant and product sections of the container which will allow pressurizing gas to mix with fluid to be dispensed and therefore will destroy the utility of the compartmenting floating piston. On the other hand, if the oxygen is slowly released by the hydrogen peroxide after sealing of the container, the rate of generation will more closely match the rate of diffusion into the foam cells and will permit pressurizing without collapse of the piston. Thus, by the detailed method a desirable piston material may be employed in pressurizing dispensers which otherwise would be useless.

Because oxygen gas generated does not ordinarily, in the preferred system illustrated, contact the fluent material being dispensed, the solubility of the gas in that material is usually inconsequential. Therefore the oxy-

gen released may be quite soluble in the aqueous or other fluid products to be dispensed and the amounts of hydrogen peroxide needed will be lower than would be required if the product and propellant portions of the dispenser were not separated. Thus, only about 1½ grams of hydrogen peroxide are needed to generate sufficient oxygen to raise the pressure of a 6 ounce standard dispenser to 7 atmospheres, 103 pounds per square inch, with the gas occupying an initial volume about half that of the container. On the other hand, where the product and propellant portions of the container are not separated, greater amounts of hydrogen peroxide will be needed when the product is one in which the oxygen gas generated is soluble. If desired, various types of corrosion inhibitors can be added to the container in small amounts, generally about up to 0.1% by weight, based on the weight of hydrogen peroxide. Such inhibitors include alkali metal silicates, such as sodium silicate. Sodium nitrite is another inhibitor which can be utilized.

The fluent material or product to be dispensed can vary widely. It can be dental cream compositions, cosmetic compositions, deodorants, various types of powders, paints, foods, such as ketchup, mustard, etc., and other types of materials such as hair sprays, etc.

The following example illustrates several forms of the invention.

Example 1

Into a standard 6 oz. drawn steel cylindrical "aerosol" container having a concave bottom sealed to it there were added in succession 3.4 grams of a 50% hydrogen peroxide solution, 0.6 gram water and 1 milliliter of 0.42% ferrous ammonium sulfate solution. An open celled polyurethane foam piston 2 inches in diameter and 1¾ inches high, of density of about 0.03 gram per cc. and average wall thickness of about 0.01 mm. was next inserted through the container on top of the hydrogen peroxide and activator. A standard dental cream or toothpaste composition was poured on top of the sponge piston. Because the resilient piston, which was coated with latex except for approximately half the area of the piston bottom, pressed against the inner container walls to separate the package into propellant and product sections, the dental cream did not flow past the piston and contact with the propellant was avoided.

No decomposition of the hydrogen peroxide was noted during the period of approximately 5 minutes in which the various sealing and filling operations were undertaken. However, on commercial mass production systems the time period is normally much less than 5 minutes, generally being less than 1 minute. Accordingly, even where down time occurs in commercial production due to faulty operation of machinery, small delays need not be of concern with respect to loss of propellant. After addition of the correct amount of dental cream, approximately 5 oz., a conventional discharge valve was staked and rolled into sealing relationship with the container top. The container was stored for 11 days after which the pressure was checked and the product dispensed. It was found that the pressure had increased to 75 lbs./sq. in. gauge and this pressure was sufficient to completely dispense the entire contents of the container. When 1 milliliter of 0.28 ferrous sulfate was used instead of the ferrous ammonium sulfate the pressure developed was 20 lbs./sq. inch gauge.

In an alternative method, the valve is first sealed to the top of an open bottom aerosol container, the can is inverted and the various components are added in the order: product, piston, mixture of propellant generator and catalytic activator, following which the concave bottom is seamed into place. When desired, one of the reactants, either propellant generator or catalytic activator, may be initially deposited on or absorbed by the piston material. However, it is usually preferable to make mixtures of propellant generator and activator in con-

centrations at which they do not immediately react, even when intimately mixed together. In such mixtures it is assured that a proportion of the propellant generator will be accessible to the activator which is needed to cause release of propellant gas.

When pistons having open celled foam structures are used, the rate of gas generation may be much greater than when the closed cell pistons are employed. Thus, to utilize a polyethylene piston of closed cell structure, one should usually control the concentrations to generate propellant gas at a rate at which it can diffuse into the cell structure. For acceptable thin walled foams, containers should not usually be brought to a pressure of over about 100 lbs./sq. inch and the pressure rise should be less than about 5 lbs./sq. inch per day.

The above invention has been described with respect to examples illustrating preferred embodiments thereof. It is not to be construed as limited to such embodiments, the scope of the invention being that set forth in the allowed claims.

What is claimed is:

1. A dispensing container having a valve and provided with a fluent material to be dispensed from the container under fluid pressure and a propellant originally comprising hydrogen peroxide as a source of oxygen, said oxygen constituting the fluid pressure-generating substance in the container, said oxygen being subsequently released from said hydrogen peroxide to generate fluid pressure, the fluid pressure generated by said release of said oxygen placing the container under a pressure sufficient to flow the material from said container through said valve when said valve is open.

2. A dispensing container as set forth in claim 1 in which said fluent material and the released oxygen are in direct contact.

3. A dispensing container as set forth in claim 1 having movable means providing two separate compartments of variable volume, one of said compartments being in communication with said valve and having said fluent material therein, and the other compartment containing said released oxygen.

4. A dispensing container provided with a discharge valve, said container containing fluent material to be dispensed and an amount of a propellant generating system comprising hydrogen peroxide and a catalytic activator therefor to controllably release oxygen gas to build up a sufficient dispensing pressure to substantially completely expel said fluent material from said container upon repeated opening and closing of said discharge valve.

5. A method of manufacturing a pressurized dispensing container comprising placing in said container at atmospheric pressure predetermined quantities of fluent material to be dispensed and of a propellant generating system comprising hydrogen peroxide to release oxygen gas and sealing said container with a discharge valve, said quantities being so predetermined that the propellant system when maintained in a sealed condition for a sufficient period of time builds up a dispensing pressure in said container at least sufficient to substantially completely expel said fluent material from said container upon repeated opening and closing of the discharge valve after the container is sealed and dispensing pressure is built up therein.

6. A method of manufacturing a pressurized dispensing container provided with a discharge valve comprising filling said container at atmospheric pressure with predetermined quantities of fluent material to be dispensed and of a propellant generating system comprising hydrogen peroxide and a catalytic activator therefor to controllably release oxygen gas and sealing said container with a discharge valve, said quantities being so predetermined that the propellant system when maintained in sealed condition for a sufficient period of time builds up a dispensing pressure in said container at least sufficient to substantially completely expel said fluent material from said con-

tainer upon repeated opening and closing of the discharge valve after the container is sealed and dispensing pressure is built up therein.

7. A dispensing container provided with a discharge valve and a floating piston of non-communicating resilient cellular structure permeable to gas and substantially impermeable to liquids and solids, said piston pressing tightly against the interior side walls of said container so as to separate the interior of said container into two compartments, one of said compartments being in communication with said discharge valve and containing fluent material to be dispensed and the other of said compartments containing an oxygen-releasing normally liquid propellant generating system comprising a solution of at least 20% by weight of hydrogen peroxide adapted to liberate oxygen propellant gas at a rate sufficiently slow to permit permeation thereof into said floating piston at a rate adequate to prevent collapse thereof on release of propellant from said propellant generating system.

References Cited in the file of this patent

UNITED STATES PATENTS

588,766 Ekenberg ----- Aug. 24, 1897

1,614,532	Mobley -----	Jan. 18, 1927
1,657,140	Wenzl -----	Jan. 28, 1928
2,120,430	Rieche -----	June 14, 1938
2,705,661	Meissner -----	Apr. 5, 1955
2,809,774	Kaye et al. -----	Oct. 15, 1957
2,815,152	Mills -----	Dec. 3, 1957
2,930,513	Zaleski -----	Mar. 29, 1960
2,954,935	Stearns et al. -----	Oct. 4, 1960
3,019,197	Saunders -----	Jan. 30, 1962

OTHER REFERENCES

Textile Colorist (Stover), pages 318, 319; Metal Catalyst for Peroxide Treatment.

Inorganic Chemistry, by Partington, MacMillan and Co., London, 1950, page 194, first paragraph of section entitled "Properties" (Of Hydrogen Peroxide).

Industrial & Engineering Chemistry, April 1956, page 748, article entitled "Concentrated Hydrogen Peroxide As a Propellant."

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,117,699

January 14, 1964

Morton Batlan Epstein

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 34, after "container" insert -- closure --; column 3, line 5, for "Gasket" read -- Gaskets --; line 68, for "stacked" read -- staked --; column 6, lines 65 and 66, for "provided with a discharge valve comprising filling said container at atmospheric pressure with" read -- comprising placing in said container at atmospheric pressure --.

Signed and sealed this 10th day of November 1964.

(SEAL)

Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,117,699

January 14, 1964

Morton Batlan Epstein

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 34, after "container" insert -- closure --;
column 3, line 5, for "Gasket" read -- Gaskets --; line 68,
for "stacked" read -- staked --; column 6, lines 65 and 66,
for "provided with a discharge valve comprising filling
said container at atmospheric pressure with" read -- comprising
placing in said container at atmospheric pressure --.

Signed and sealed this 10th day of November 1964.

(SEAL)

Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents