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METHOD OF PRESSURE PACKAGING PRODUCTS HAVING A PETROLEUM BASE

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METHOD OF PRESSURE PACKAGING PRODUCTS
HAVING A PETROLEUM BASE
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This invention relates to a method for filling pressure packages sometimes referred to as aerosol dispensers. More particularly, the invention relates to a method of filling pressure packages utilizing a noncondensible gas.

Two types of propelent are used in the filling of pressure packages, the so-called condensible and noncondensible gases. The words "condensible" and "noncondensible" as used in this context are relative terms since all gases liquefy or solidify under extreme conditions of temperature and pressure. These terms are used herein in the manner in which they are commonly used in the pressure packaging industry, the word "condensible gas" is used to refer generally to those products which are liquefiable under ordinary temperatures and pressures. Included among the noncondensible gases are nitrogen, carbon dioxide and hydrogen. Typical of the condensible gases are the lower molecular weight hydrocarbons, such as isobutane and n-butane, and the fluorocarbons such as chlorotrifluoromethane and dichlorodifluoromethane commonly known as Propellents 11 and 12 respectively.

The differences in these two types of gas reflect in some extent upon the performance of the products which they are used to dispense. Condensible gases, frequently referred to as liquefied propelents, are injected into the containers filled with the product to be dispensed in liquefied state. An equilibrium is established between the liquefied phase of the propelent and the gaseous phase of the propelent in the headspace of the container. When the container valve is opened, the gaseous portion of the propelent acts as a piston driving the product to be dispensed downwardly, and up and out through the dip tube. As this occurs, the pressure in the headspace may be temporarily reduced, but if so, it is almost immediately re-established by vaporization of some of the liquefied propelent into the gaseous phase. As long as any propelent remains in the liquefied phase, the pressure in the headspace remains relatively constant thereby driving the product out of the package with constant force when the valve is opened.

In contrast, a product packaged with a noncondensible gas contains propelent principally in the gaseous phase. A limited amount of the noncondensible gas may be soluble in the product phase. The gas is normally injected into the container where it remains in the headspace thereof until the container is emptied of product. As part of the product is emitted from the container, the remainder occupies less space leaving a greater space to be occupied by essentially the same amount of propelent. Thus, the pressure in the headspace diminishes as the product is dispensed, a factor which is taken into consideration when determining the amount of propelent needed. Some of the noncondensible gas which has become solubilized in the product phase will come out of solution and enter the headspace to partially rebuild the pressure in the headspace. The extent to which this phenomenon occurs will depend principally on the solubility of the noncondensible gas in the product phase and the existing pressure in the headspace.

As indicated above, two types of propelent have been used in filling pressure packages— the condensible and noncondensible gases. Turning now to filling methods, three distinct procedures have been employed, namely, cold filling, through-the-valve filling, and under-the-cap filling.

Cold filling comprises chilling or refrigerating both the concentrate and the propelent, injecting them into the container while chilled and thereafter inserting and securing the valve assembly and closure in place. This method of filling requires refrigeration equipment and is therefore expensive. Many solutions are adversely affected by refrigeration.

In filling through the valves, all of the product ingredients are placed in the container. The valve closure is secured in place and thereafter, the propelent is injected into the container through the valve. A few of the less volatile propelents, such as trichlorofluoromethane, which are commonly used in combination with more volatile propelents, such as dichlorodifluoromethane, may be placed in the container with the product phase, with the more volatile component of the propelent combination injected through the valve. Pressure packaging by filling through the valve does not require refrigeration. However, since the valve passage requirements may be relatively small or the amount of propelent large, considerable time is required to get the required amount of propelent into the container.

Of the three methods of filling pressurized packages, the under-the-cap method is the latest to become commercially utilized. This method permits the filling of the container with both product and propelent at room temperature with greater speed and economy than is possible using the through-the-valve method. By this method, utilizing filling equipment such as that disclosed in United States Patent 2,947,126, a measured quantity of the active ingredient is first placed in the container. The cap, with valve and operating button attached, is then loosely placed over the top opening of the can after which a closed chamber is formed about the above the container-top opening. The container cap closure including the valve and attached operator button is elevated from engagement with the container top opening, and when this is accomplished, a measured amount of a condensible propelent in liquid form, such as dichlorodifluoromethane is introduced instantaneously into the container through the uncovered open top thereof. The cap, valve and operator button are immediately replaced as an assembled unit and sealed into position, thereby completing the operation.

In summary, pressure packages have been filled by three methods, cold filling, through-the-valve filling and under-the-cap filling. Condensible or liquefiable propelents only, such as isobutane and halogenated hydrocarbons, have been used in the cold filling and the under-the-cap methods, while both condensible and noncondensible gases have been used in the through-the-valve method.

Condensible gases are not without advantages as propelents for pressure packages. However, noncondensible gases possess several advantages over condensible gases. Noncondensible gases are considerably less expensive than condensible gases. Noncondensible gases possess solubility in dichlorodifluoromethane and dichlorotetrafluoroethane. Noncondensible gases do not liquefy under ordinary temperatures and pressures. Consequently, they may be used to generate a wide variety of pressures without dilution simply by essentially varying the amount of gas compressed in the headspace of a container. A condensible gas, on the other hand, generates a given pressure after liquefication at ambient temperatures which can be modified only by blending it with other liquefied gases or other diluents. Further, a greater product-to-propelent ratio can be established with a noncondensible gas since only a small amount is required to do the job.

With all of their advantages, noncondensible gases possess many disadvantages which have seriously impeded their adoption for use in pressure packaging. Carbon
dioxide reacts rapidly with water to form carbonic acid which attacks metal containers leading to corrosion and leakage problems and is incompatible in anionic emulsion systems. Hydrogen is highly explosive and has been given little consideration as a commercial propellant. Nitrogen exhibits such a low degree of solubility in most liquids that its effectiveness as a propellant is seriously affected after a few initial uses of a product pressurized with it. Nitrous oxide, although not flammable itself, supports combustion and therefore may present a safety problem when handling large amounts of petroleum distillate in its presence.

It has now been discovered that carbon dioxide can very effectively be used to pressure a specialized line of products, namely water free petroleum based insecticidal products, and that pressure packages may be rapidly filled with water free petroleum based insecticidal products and carbon dioxide by a novel process utilizing the under-the-cap method, thus avoiding the use of refrigeration necessary to the cold filling process and the bottle-necks which accompany filling through-the-valve.

There are now on the market several pressurized petroleum based insecticidal products. Typical of these are the dried ant killers and moth provers. Due to the flammability of the petroleum base of these products, the manufacturers have chosen to package them almost exclusively with halogenated propellents such as the Freons and Genetrons which are non-flammable and will not support combustion. It has now been discovered that carbon dioxide possesses unique advantages when used to propel water free petroleum based insecticidal products in accordance with the method of the present invention. By eliminating water from the products packaged, no carbonic acid which could cause container corrosion is formed. Also, carbon dioxide is not flammable itself and does not support combustion therefore making it perfectly safe to use in combination with flammable petroleum based products.

Another advantage in the use of a carbon dioxide to propel petroleum based insecticidal products resides in the fact that carbon dioxide is soluble to a substantial degree in the petroleum distillate base of these products. In this respect carbon dioxide differs greatly from other non-condensable gases such as nitrogen which is only slightly soluble in petroleum distilling. The advantage afforded due to the solubility of carbon dioxide in the petroleum base, is that after each use of the packaged product the pressure within the head space is re-established to an appreciable degree by the establishment of a new equilibrium between the gas in the head space and that dissolved in the petroleum distillate, part of the gas escapes from the petroleum distillate into the container head space. This phenomenon would not occur if the carbon dioxide were not soluble in the petroleum base of the product.

The most obvious method of pressurizing a petroleum based insecticidal product with carbon dioxide once such a combination of ingredients were formulated or ingeniously decided upon would be to place the product in the container and then inject carbon dioxide through the valve stem into the head space of the container. Alternately, one might be expected to dissolve the propellant in the entire concentrate and then transfer the entire product under pressure to the containers from which it is to be dispensed.

To follow the first of the above methods of filling a container with petroleum base and a carbon dioxide propellant would be very time consuming since it would require forcing all of the propellant through the valve stem into the container. Also, to get the required amount of carbon dioxide in the container to dispense it in an appropriate spray throughout the life of the product would require an extremely high initial pressure within the container. This is true because the carbon dioxide is not immediately soluble in petroleum distillate but requires some time for an equilibrium to be established.

All of the difficult problems in the pressure packaging of petroleum based insecticidal products may be overcome by the present process while utilizing the economical and otherwise very desirable condensable gas, carbon dioxide. The process involves providing a charge of carbon dioxide, dissolving all of the ingredients making up the product except the propellant, commonly called the insecticidal ingredients and a part of the petroleum distillate, and the second portion of the concentrate comprising the balance of the petroleum distillate; depositing the first portion of the concentrate in a container, dissolving the carbon dioxide in the second portion of the concentrate; thereafter injecting the second portion of the concentrate having carbon dioxide dissolved therein into the container; and then sealing the container with a closure comprising a valve assembly through which the product may be emitted under pressure.

When pressure packaging with a condensable gas it is desirable to purge the container of air since the mixture of air and propellant utilized may otherwise produce undesirable erratic spray patterns due to the varying solubilities of the gases in the product being dispensed. By the present method, the container is partially filled prior to the introduction of the propellant into the container. This results in less space to be purged of air before introduction of the propellant and therefore prevents a distinct advantage over the alternate possible filling method discussed above. Thus, the propellant is dissolved in the entire concentrate and then transferred under pressure to the containers from which it is to be dispensed.

Also the present method permits great economy and speed of operation since the first portion of the concentrate may be deposited in one set of containers while the second portion of the concentrate, namely the remainder of the petroleum distillate, to which carbon dioxide has been added, is injected into other containers already filled with the first portion of the concentrate. Dividing the petroleum distillate in two portions, as in the present process also eliminates the necessity of passing the entire product through an impregnator or other equipment for dissolving the noncondensable gas in it.

By dissolving the carbon dioxide in a second portion of the petroleum base, as in the present invention, and introducing it into the container as a liquid, less initial pressure exists in the container than would be the case if the carbon dioxide were introduced in its gaseous phase following the introduction of all of the petroleum distillate. During this process, carbon dioxide is already dissolved in the petroleum distillate with which it is admitted. Following the more obvious method of placing the entire concentrate in the container followed by the gaseous propellant would require that enough carbon dioxide be introduced in the container under pressure high enough to permit a sufficiently high final pressure after an equilibrium is established between the gaseous phase in the head space and the carbon dioxide dissolved in the petroleum distillate. It is well known that the less pressure a container must withstand the cheaper it can be manufactured other factors being equal.

The present process is also cheaper and more efficient for another but related reason. In the packaging of pressurized products, the filled containers charged with propellant are submerged in accordance with Interstate Commerce Commission regulations into a tank of water maintained at least 130°F, commonly called a "hot tank" as a quality control measure to screen out any containers which may already be defective or which became defective when subjected to the increased pressure developed due to the increased temperature. A product charged with a gaseous propellant must be vigorously shaken for a prolonged period of
time before being subjected to this hot tank treatment to effect as complete a solubilization as possible of the propellent in the liquid carrier. Otherwise, pressure would be built up in the containers during the hot tank treatment far beyond that which it is necessary for them to withstand during any reasonably foreseeable conditions of use. Since in the practice of the present process, the gaseous propellent is solubilized in a substantial portion of the total product before it is placed in the container, the initial pressure is lower than it would otherwise be and shaking of the filled and charged container is eliminated.

Petroleum distillates will be present in the insecticidal concentrate of the invention in an amount between about 40% and about 99.5% by weight.

The petroleum distillates which may be used in practicing the invention include naphtha, gasoline, kerosene, benzine, mineral seal oil, paraffin oil and the like. Additional solvents and diluents such as isopropanol, ethanol and methylene chloride may also be present. Naphtha, kerosene, and mineral spirits are preferred petroleum distillates.

Any insecticidal ingredient which is soluble or substantially soluble in the selected petroleum distillate may be used. The following are presented as a partial list of insecticidal agents which may be used: dieldrin (hexachloro-epoxy-octahydro dimeta nonapthalene) chlor dane (octachloro-4,7 methano tetra hydroindane) diethyl diphenyl dichloroethane, paradelchlorobenzene, methoxychlor (1,1,1-trichloro-2, 2-bis para-methoxyphenyl ethane), DDT (dichloro-diphenyl-trichloroethane) DDD (2,2-bis para-chlorophenyl -1,1 dichloroethane), Captan (N-trichloromethylcercapto, cyclo hexene -1 ,2 dicarboximide), Karathane (a mixture of difluro methylethyl phenyl cyanate and difluro methylethy phenyl phenol), piperonyl butoxide (butyl carbyl) (6-propyl piperyln) and rotenoids. Dieldrin and chlor dane are preferred in products for killing roaches and ants. Diethyl diphenyl dichloroethane is preferred in products for killing or mitigating mites. Those skilled in the art will recognize that other insecticidal agents may be effectively used in the invention.

The amount of active ingredient to be carried by the petroleum distillate will depend on the purpose for which the product is intended, the nature of the active insecticidal ingredient, and the solubility of the ingredient in the petroleum distillate. Usually, the active ingredient will be present in an amount ranging from about 0.5% and about 5% by weight of the concentrate, that is of the total product, the carbon dioxide propellant omitted.

The carbon dioxide will be dissolved in that portion of the petroleum distillate which is added to the container as a second portion of the product in an amount ranging from about 2% to about 15% by weight of the petroleum distillate in which it is dissolved. This may be accomplished by any desired technique such as bubbling the carbon dioxide through the petroleum distillate by use of a sparger or by spraying the petroleum distillate through a carbon dioxide atmosphere under controlled temperature and pressure conditions. When the spray method is used the temperature of the petroleum distillate and pressure of the nitrous oxide may be varied widely between about 0°F and about 150°F and about 5 and about 50 atmospheres gauge respectively. Preferably the petroleum distillate will be maintained at a temperature of between about 0°F and about 90°F and the pressure of the carbon dioxide between about 8 and about 14 atmospheres gauge.

The amount of petroleum distillate to be used in the first portion of the concentrate, which is deposited in the container prior to the addition of the final portion of distillate containing carbon dioxide, may vary from about 25% to about 75% by weight of the total amount of petroleum distillate in the final insecticidal product.

The following examples are presented to illustrate the invention.

Example 1

A pressurized insecticidal product for killing roaches, ants and miscellaneous other insects was prepared according to the following formula as hereafter described:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Percent by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorodane</td>
<td>2.00</td>
</tr>
<tr>
<td>Pyrethrins</td>
<td>0.05</td>
</tr>
<tr>
<td>N-octyl bicycloheptene dicarboxyimide</td>
<td>0.15</td>
</tr>
<tr>
<td>Piperonyl butoxide</td>
<td>0.10</td>
</tr>
<tr>
<td>Petroleum distillate</td>
<td>94.95</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>2.75</td>
</tr>
</tbody>
</table>

All of the active ingredients in the above formula were dissolved in 45% by weight of the specified amount of petroleum distillate. This concentrated solution represented the first portion of the concentrate as that term is used in the present invention. Several 16 ounce cylindrical metal containers were filled, each with 5 ounces of this concentrated solution using a conventional piston filler and with 7 ounces of petroleum distillate saturated with carbon dioxide using an under-the-cap filling machine of the type disclosed in United States Patent 2,947,126 issued to Focht.

The petroleum distillate solution of carbon dioxide was prepared and delivered to the under-the-cap filler by use of a system shown in the drawings. This system and its operation will now be described.

Hot and cold petroleum distillate are introduced into conduits 11 and 12 respectively and passes through re-mo re controlled valves 13 and 14, where the rate of passage is regulated by temperature regulator 15. Temperature regulator 15 is suitably connected with conduits 11 and 12 at their junction 18 through a sensitizing element 17 positioned at the junction and connecting means 16, and electrically connected with remote controlled valves 13 and 14 through connections 19 and 20. Temperature regulator 15 responds to the temperature of the petroleum distillate passing from conduits 11 and 12 past junction 18 and its own setting to adjust remote controlled valves 13 and 14 to maintain the petroleum distillate at the desired temperature.

Petroleum distillate at controlled temperatures, formed by the mixture of hot and cold distillate at junction 18, flows through conduit 21 and remote controlled valve 22 into the head space of vacuum deaerating unit 23 where it is dispensed downwardly in a fine spray through spray head 24. Provision is made for draining conduits and passage is regulated by level control unit 28 which in turn is suitably connected through conduit 29 and 30 to vacuum deaerating unit 23 at different vertical positions 31 and 32. The input of petroleum distillate through spray head 24 is regulated by the level control unit 28 and remote controlled valve 22 so that a distillate level 33 is maintained in the deaerating unit 23 between elevations 31 and 32. The vacuum deaerating unit 23 is equipped with a vacuum gauge 34 and means for draining the vacuum deaerating unit are provided through conduit 51 and valve 56.

The vacuum deaerator 23 is connected at a position above the petroleum distillate level with a vacuum pump, not shown, through vacuum conduit 37. The vacuum deaerator 23 is also connected in parallel at a position below the distillate level through conduits 40, 41 and 42 with feed pumps 43 and 44. Feed pumps 43 and 44 are in turn connected through conduit 45 with an impregnating tank 46 where deaerated petroleum distillate from the vacuum deaerator 23 is impregnated with carbon dioxide. Conduit 45 is equipped with a pressure relief valve 47 and a remote controlled valve 48.
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A level control unit 49 similar to level control unit 28 is connected to the impregnator 46 at positions 50 and 51 through connecting means 52, 53 and 54. The flow of petroleum distillate from the vacuum deaerator 23 through conduit 45 is thus controlled by level control unit 49 and remote controlled valve 48 so that it is dispensed upwardly through spray head 54 at an appropriate rate to maintain the distillate level 55 between position 50 and 51.

The impregnator 46 is connected through conduit 60 equipped with shut-off valve 61 to vacuum conduit 37 connected with a vacuum generator not shown. This connection permits air to be pulled out of the impregnator prior to introduction of carbon dioxide and petroleum distillate into the impregnator. Mounted in the upper portion of impregnator 46 are a pressure safety valve 62 and a purging means comprising conduit 63 and valve 64.

Below the petroleum distillate level there is mounted in the impregnator 46 a sample top 65, drain means 66, low level detector 67 and agitating means 68 equipped with a motor 69 and propeller shaft 71.

Carbon dioxide from a supply station not shown enters into top of impregnator 46 under pressure through conduit 72. The pressure under which the non-condensable gas enters the impregnator is controlled by pressure-sensitive element 75 inside the impregnator 46 connected to pressure control unit 73 through pressure sensitive conductor 74 and to remote control valve 76 through electrical connecting means 77.

Depending upon the type of pressure control unit used at 73, it may be necessary to place a step-down pressure regulator, not shown, in conduit 72. To maintain the petroleum distillate in the impregnator 46 at a desired temperature, a heat exchanger 78 is provided. The heat exchanger 78 is connected to the impregnator below the liquid level through conduit 79 and pumps 80 and 81 connected in parallel by conduits 82 and 83. Petroleum distillate flowing from the impregnator 46 into the heat exchanger 78 re-enters the impregnator above the distillate level through conduit 84 and spray head 85.

A temperature controlling and recording unit 90 is mounted between the heat exchanger 78 and impregnator 46. Temperature sensitive unit 91 is mounted in the impregnator below the petroleum distillate level and connected to recorder 90 through connecting means 92. The temperature recorder is also connected with remote control valve 93 through electrical connecting means 94 mounted in conduit 94. Conduit 94 is connected to a cold water supply not shown. Cold water entering heat exchanger 78 through conduit 94 leaves the exchanger through conduit 94e. Conduit 95 connects vacuum deaerator 46 with parallel pumps 96 and 97 which in turn are connected to conduits 98 and 99 through which the petroleum distillate impregnated with carbon dioxide flows toward its intended use. Valves 100 and 101 are connected to the impregnator 46 through conduits 102, 103, and 104 to permit recovery of the carbon dioxide solution into impregnator 46 in the event that the solution flow through conduit 105 is stopped while pumps 96 or 97 continue to run. Conduits 98 and 99 merge into a single conduit 105 at a position beyond the by-pass valves 106 and 101. Conduit 105 carrying carbon dioxide-impregnated petroleum distillate under pressure is delivered to an under-the-cap filling machine of the type disclosed in Focht Patent 2,947,904.

In the process of packaging the product of Example I, a vacuum pump was connected to conduits 37 and 60 with valve 61 in open position. After a vacuum of 15 inches of mercury was obtained, impregnator 46, petroleum distillate maintained at a temperature of 70 °F. by temperature control regulator 15 was introduced into the vacuum deaerator 23 through conduit 21 and spray head 24. Valve 61 was closed and carbon dioxide maintained at a pressure of 70 p.s.i.g. by pressure control unit 73 was introduced into the top of impregnator 46.

After deaerated petroleum distillate accumulated in the vacuum deaerator 23 to a level between positions 31 and 32 and the carbon dioxide had reached a pressure of 70 p.s.i.g., impregnator 46, pump 43 or 44 was started and deaerated petroleum distillate pumped into impregnator 46 through conduit 45 and spray head 54. Addition of the petroleum distillate to the impregnator 46 increased the carbon dioxide pressure therein to about 170 p.s.i.g. Carbon dioxide prevailing in the headspace of impregnator 46 became dissolved in the petroleum distillate as the petroleum distillate was sprayed through it. After several inches of petroleum distillate impregnated with carbon dioxide had accumulated in the bottom of impregnator 46, it was recycled through heat exchanger 78. This was accomplished by starting pump 80 or 81 which pumped carbon dioxide impregnated petroleum distillate from the bottom of impregnator 46 through conduit 84 and spray head 85. Recirculation of the carbon dioxide impregnated petroleum distillate served to maintain the temperature of the liquid in the impregnator 46 at a temperature of 70 °F. and to further expose the petroleum distillate in the form of a fine spray to additional compressed carbon dioxide in the head space of impregnator 46 thereby increasing and stabilizing the amount of carbon dioxide dissolved in the petroleum distillate. After approximately 5% by weight of carbon dioxide became dissolved in the water maintained at 70 °F. under carbon dioxide pressure of 170 p.s.i.g. pump 96 or 97 was started causing the carbon dioxide impregnated petroleum distillate to flow from the bottom of impregnator 46 through conduits 95 and 98 and 99 into conduit 105 connected with under-the-cap filling machine of the type described in United States Patent 2,947,126 to Focht. There a measured amount of petroleum distillate impregnated with carbon dioxide was injected into each of the several containers as the final component of the insecticidal product, the formula of which is presented at the beginning of the example. The pressure of each of the containers filled in this manner was checked immediately after filling and found to have a gauge pressure of approximately 80 p.s.i.g.

The contents of several of the containers packaged in this manner were totally dispersed at intermittent periods from the containers while observing the spray patterns. Excellent spray patterns were produced until the last of the liquid was dispensed from the containers. Although pressure within the containers dropped from about 80 p.s.i. to about 40 p.s.i. while the contents were being dispensed, no appreciable difference in spray pattern was observed.

Example II

Another pressurized insecticidal product formulated particularly for killing moths and related insects was prepared according to the following formula: diethyl diphenyl dichloroethane and related reaction products 5.0% by weight; petroleum distillate 92.3% by weight, and carbon dioxide 2.7% by weight. The active ingredient, diethyl diphenyl dichloroethane, was dissolved in 42% by weight of the specified amount of petroleum distillate. The concentrated petroleum distillate solution of the active ingredient represented the first portion of the product concentrate. Several 16-ounce cylindrical metal containers were filled each with 5 ounces of this concentrated solution using a conventional piston filler. Thereafter 7 ounces of petroleum distillate saturated with carbon dioxide were deaerated at 10 °F. and added using an under-the-cap filling machine of the type disclosed in United States Patent 2,947,126 to Focht. These packages, like those of Example I, gave excellent
spray patterns throughout their life and the product functioned effectively as a moth proofer.

From the foregoing it will be seen that a new method of pressure packaging a specific line of pressurized products has been developed by which those products can be more economically packaged than in the past.

It will be appreciated by those skilled in the pressure packaging of insecticidal products that limited changes can be made in the present invention without departing from its spirit. Having described the invention,

What is claimed is:

1. A method of filling an aerosol container with a water-free insecticidal composition containing carbon dioxide propellant, insecticide and petroleum distillate which comprises depositing in said container the insecticide and a first portion of petroleum distillate which is substantially free from carbon dioxide and subsequently adding under pressure to said container a second portion of petroleum distillate which contains carbon dioxide dissolved therein.

2. A method according to claim 1 wherein the second portion of petroleum distillate is obtained from a deaerated petroleum distillate fraction which has been sprayed through an atmosphere of carbon dioxide.

3. A method according to claim 2 wherein the second portion of petroleum distillate is sprayed at a temperature from about 0° F. to about 150° F. through carbon dioxide under pressure from about 5 to about 50 atmospheres.

4. A method according to claim 1 wherein the carbon dioxide is present in the second portion of petroleum distillate in a concentration of from about 2% to about 15% by weight.

5. A method according to claim 1 wherein the water-free insecticidal composition contains from about 0.5 to about 5% by weight insecticide and from about 40% to about 99% by weight petroleum distillate.

6. A method according to claim 5 wherein the insecticide is selected from the group consisting of chlordane, dieldrin, pyrethrum, and diethyl diphenyl dichloroethane.

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