# United States Patent [19]

## **Butler**

## [54] PROPELLANTS AND REFRIGERANTS BASED ON TRIFLUOROPROPENE

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- [51] Int. Cl..... C09k 3/30; C09k 3/06; F25 9/00

## <sup>[11]</sup> **3,884,828**

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# [56] **References Cited**

	OBUIED	STATES FATENIS
3,067,263	12/1962	Newport et al 260/653.3
3.583.921	6/1971	Healy et al 252/90

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## [57] ABSTRACT

Aerosol propellants and refrigerants based on trifluoropropene ( $CF_3CH=CH_2$ ) are disclosed.

10 Claims, No Drawings

### PROPELLANTS AND REFRIGERANTS BASED ON TRIFLUOROPROPENE

This invention relates to an aerosol product which includes a propellant wherein the improvement comprises employing trifluoropropene as 1 to 100 percent 5 by weight of the propellant.

This invention also relates to a refrigeration system in which the refrigerant undergoes a change from the liquid to the vapor state wherein the improvement comprises employing trifluoropropene as 1 to 100 percent by weight of the refrigerant. stance called the refrigerant is ca physical change. The most widely u is that in which the refrigerant u from the liquid to the vapor state. Trifluoropropene can be used as

With the ever increasing number of aerosol products being marketed there is an increasing demand for new propellants to solve the problems encountered in dispensing the materials and to meet the needs involved 15 with specific products and uses.

Similarly, with improvements in existing refrigeration systems, and the designing of new refrigeration systems, there is an increasing demand for new refrigerants which will function satisfactorily.

Most aerosol products contain three major components. These are the active ingredient, the solvent and the propellant. While these components have been referred to in the singular, it is believed obvious that each "component" can consist of more than one ingredient. 25 One aspect of the present invention is directed to the propellant used in aerosol products. It has been found that trifluoropropene can be employed as 1 to 100 percent by weight of the propellant. That is, trifluoropropene can be used alone as the propellant in an aerosol or it can be used in combination with other propellants in an aerosol. It should be noted at this point that while the function of the trifluoropropene is basically and primarily that of a propellant that it may also perform an incidental function as a solvent and this is within the scope of the term propellant as used in this specification and claims.

The propellant provides the pressure that forces the aerosol product from the container when the valve is opened. Also, the propellant has an influence on whether the product is discharged in the form of a spray, stream, or as a foam. Variations in the propellant can also influence, for example, whether one obtains a course or fine spray or whether one obtains a good or poor foam. Thus it can be seen that the discovery that trifluoropropene can be employed as a propellant gives the aerosol manufacturer greater latitude in preparing products than heretofore available to him.

As noted above, trifluoropropene can be used as the sole propellant or in combination with other known propellants. Examples of suitable propellants which can be employed in combination with trifluoropropene include fluorodichloromethane, difluorochloromethane. fluorotrichloromethane. difluorodichloromethane, 1,2,2-trifluoro-1,1,2-trichloroethane, 1,1,2,2tetrafluoro-1,2-dichloroethane, 1,1,2,2,2-pentafluoro-1,1-difluoro-1-chloroethane, 1-chloroethane, 1.1difluoroethane, octafluorocyclobutane, methylene chloride 1,1,1-trichloroethane, tetrafluoroethylene, 6 vinyl chloride, propane, n-butane, isobutane, ethylene, dimethyl ether, nitrogen, nitrous oxide, carbon dioxide and mixtures thereof. It will be noted from the examples given that the trifluoropropene can be employed in combination not only with other liquified gas propel-65 lants but also in combination with compressed gas propellants. No meaningful limitations can be set as to the relative proportions of the individual propellants to be

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used in combination as this depends on the individual needs and the particular product being formulated.

Another aspect of this invention is the use of trifluoropropene as a refrigerant. The most common refrigeration systems today are designed to carry out a process for producing cold in which a working substance called the refrigerant is caused to undergo a physical change. The most widely used physical change is that in which the refrigerant undergoes a change from the liquid to the vapor state.

Trifluoropropene can be used as the sole refrigerant in a system or it can be used in combination with other refrigerants. By way of illustration, trifluoropropene can be used in admixture with fluorodichloromethane, difluorochloromethane, fluorotrichloromethane, difluorodichloromethane, 1,2,2-trifluoro-1,1,2trichloroethane, 1,1,2,2-tetrafluoro-1,2dichloroethane, 1,1,2,2,2-pentafluoro-1-chloroethane, 1,1-difluoro-1-chloroethane, 1,1-difluoroethane, octa-20 fluorocyclobutane, methylene chloride, 1.1.1trichloroethane, tetrafluoroethylene, vinyl chloride, propane, n-butane, isobutane, ethylene, dimethyl ether, nitrogen, nitrous oxide, carbon dioxide and mixtures thereof. No meaningful limitations can be set as to the proportions to be used as the choice of a refrigerant for a specific application is determined by the thermodynamic properties, physical properties and chemical properties needed for that application.

Now in order that those skilled in the art may better 30 understand how the present invention can be practiced, the following examples are given by way of illustration and not by way of limitation. Trifluoropropene has a boiling point of about -22°C. and a vapor pressure of approximately 60 pounds per square inch gauge (psig) 35 at 25°C. Trifluoropropene is flammable, and acute studies indicate it to be relatively non-toxic. All percents referred to herein are by weight unless otherwise specified.

### Example 1

Prior to the actual preparation of any aerosol products it was desirable to know the vapor pressure of the propellant to be used. To obtain this information varying percentages of trifluoropropene and 1,1,1trichloroethane (Chlorothene) were placed in aerosol cans and the vapor pressures measured at 70°F. The results of these measurements are set forth in the following table. These results show that trifluoropropene can be used in combination with other propellants for making aerosol products.

	. P	Vapor Pressure	
5	Trifluoropropene	1,1,1-trichloroethane	(psig)
.0	10	90	20
	20	80	31
	30	70	41
	40	60	49
	50	50	54
	60	40	60
	70	30	67
	80	20	71
	90	10	82

### Example 2

Six units of three different aerosol products were packaged using trifluoropropene as the propellant.

Two control units were prepared for purpose of comparison with each set and were identical in every respect except that difluorodichloromethane was used as the propellant. The aerosol products were a release agent for cooking utensils (Pan Shield), a water repel- 5 lent agent for leather goods (Shoe Saver), and a textile treating agent (Fabriglide). Three units and one control of each set were stored at room temperature and three units and one control were stored at 100°F. The first examples (one from room temperature and one 10 from 100°F.) were opened and examined after two weeks, the second samples were checked a month later, and the final samples with controls a month after that. After 2½ months of shelf-life all products were stable with no deviations from the control units. There was no 15 dichloroethane, 1,1,2,2,2-pentafluoro-1-chloroethane, change in the product color nor any attack on the aerosol container. Pressures remained relatively constant, and weight losses were negligible. It was noted that the trifluoropropene had a light characteristic odor which could be masked with perfume if found objectionable. 20

Although the vapor pressure of trifluoropropene is lower than that of difluorodichloromethane, in combination with such materials as 1,1,1-trichloroethane, currently available data indicates that it gives a slightly higher pressure than that of similar difluorodi- 25 chloromethane combinations. Therefore, that data indicates that it is possible to use less trifluoropropene than difluorodichloromethane in an aerosol product to attain the desired pressure.

#### Example 3

When the following propellants are substituted for trifluoropropene in the aerosol products of Example 2, similar results are obtained:

4.4		
(A)	1%	trifluoropropene
· /		difluorodichloromethane
(B)	50%	trifluoropropene
	50%	1,1,1-trichloroethane
(C)		trifluoropropene
		fluorotrichloromethane
(D)		trifluoropropene
	35%	1,1,2,2-tetrafluoro-1,2-dichloroethane
(E)		trifluoropropene
	20%	1,2,2-trifluoro-1,1,2-trichloroethane
(F)		trifluoropropene
		vinyl chloride
(G)		trifluoropropene
		fluorotrichloromethane
		dimethyl ether
(H)		trifluoropropene
		fluorotrichloromethane
		isobutane
(I)		trifluoropropene
	9%	propane

#### Example 4

When the following refrigerants are used in a refrigeration system in which the refrigerant undergoes a 55 change from the liquid to the vapor state, such as the refrigeration systems found in refrigerators and freezers, good cooling is obtained:

(A)	100%	trifluoropropene
(B)	90%	trifluoropropene
	10%	difluorodichloromethane
(C)	80%	trifluoropropene
	20%	1,2,2-trifluoro-1,1,2-trichloroethane
(D)		trifluoropropene
	50%	fluorotrichloromethane
(E)		trifluoropropene
		fluorotrichloromethane
	10%	isobutane

-Continued 1% trifluoropropene 99% fluorotrichloromethane

That which is claimed is:

1. In an aerosol product which consists essentially of an active ingredient, a solvent and a propellant in a container, the improvement comprising employing trifluoropropene as 1 to 100 percent by weight of the propellant, the balance of the propellant being selected from the group consisting of fluorodichloromethane, difluorochloromethane, fluorotrichloromethane, difluorodichloromethane, 1,2,2-trifluoro-1,1,2trichloroethane, 1,1,2,2-tetrafluoro-1,2-

1,1-difluoro-1-chloroethane, 1,1-difluoroethane, octamethylene fluorocyclobutane, chloride, 1.1.1trichloroethane, tetrafluoroethylene, vinyl chloride, propane, n-butane, isobutane, ethylene, dimethyl ether, nitrogen, nitrous oxide, carbon dioxide and mixtures thereof.

2. An aerosol product as defined in claim 1 wherein trifluoropropene constitutes 100 percent of the propellant.

3. An aerosol product as defined in claim 1 wherein the trifluoropropene constitutes less than 100 percent of the propellant.

4. An aerosol product as defined in claim 3 wherein the trifluoropropene constitutes less than 100 percent  $_{30}$  of the propellant, and the balance of the propellant is 1,1,1-trichloroethane.

5. An aerosol product as defined in claim 3 wherein the trifluoropropene constitutes less than 100 percent of the propellant, and the balance of the propellant is 35 fluorotrichloromethane.

6. An aerosol product as defined in claim 3 wherein the trifluoropropene constitutes less than 100 percent of the propellant, and the balance of the propellant is 1,1,2,2-tetrafluoro-1,2-dichloroethane.

7. An aerosol product as defined in claim 3 wherein 40 the trifluoropropene constitutes less than 100 percent of the propellant, and the balance of the propellant is 1,2,2-trifluoro-1,1,2-trichloroethane.

8. In a process of expelling an aerosol product which 45 consists essentially of an active ingredient, a solvent and a propellant from a container by means of the propellant the improvement comprising employing as the propellant a composition consisting essentially of from 1 to 100 percent by weight of trifluoropropene, the bal-

50 ance of the propellant being selected from the group consisting fluorodichloromethane, of difluorochloromethane, fluorotrichloromethane, difluorodichloromethane, 1,2,2-trifluoro-1,1,2-trichloroethane, 1,1,2,2-tetrafluoro-1,2-dichloroethane, 1,1,2,2,2pentafluoro-1-chloroethane, 1.1-difluoro-1chloroethane, 1,1-difluoroethane, octafluorocyclobutane, methylene chloride, 1,1,1-trichloroethane, tetrafluoroethylene, vinyl chloride, propane, n-butane, isobutane, ethylene, dimethyl ether, nitrogen, nitrous oxide, carbon dioxide and mixtures thereof. 60

9. A process as defined in claim 8 wherein the trifluoropropene constitutes 100 percent of the propellant.

10. A process as defined in claim 8 wherein the tri-65 fluoropropene constitutes less than 100 percent of the propellant.

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