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## EMULSION CONTAINING A LIQUEFIED PROPELLANT GAS UNDER PRESSURE AND METHOD OF SPRAYING SAME

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This invention relates to self-propellant emulsions of a liquid composition which it is desired to spray and a liquefied gas, and to a method of spraying in which such emulsions are used.

It already has been proposed to form self-propellant spraying compositions by dissolving a liquefied gas in a liquid to be sprayed. I have found, at least with respect to the spraying of many liquids, that superior results are obtained if the liquid to be sprayed and the liquefied gas to form the expelling force during spraying are immiscible, or are soluble in one another only to a limited extent, and are formed into an emulsion, as distinguished from a solution.

Emulsions generally are classified as being either of the water-in-oil type or of the oil-in-water type, "water" in such cases and herein being used to define any polar substance and "oil" to define any non-polar substance. In a water-in-oil emulsion, the water is present in the form of small droplets dispersed in a continuous oil phase. In an oil-in-water emulsion, the oil is present in the form of small droplets dispersed in a continuous water phase. Emulsions also may be formed of two polar substances, or two non-polar substances provided they are immiscible or relatively so. Also, emulsions can be formed by emulsifying an oil-in-water emulsion in a continuous oil phase; by emulsifying a water-in-oil emulsion in a continuous water phase; by dispersing a gas in a liquid; or by distributing liquid particles in a gas. However, the latter, known as "aerosols," are, strictly speaking, dispersions rather than emulsions.

The present invention contemplates any of the above types of emulsions, as long as one constituent thereof is a liquefied gas, the term "liquefied gas" being used herein to define any liquid having a boiling point below that of the prevailing temperature of the atmosphere, at atmospheric pressure, although I prefer to use a liquefied gas having a boiling point below 0° C. However, in the spraying of my liquids the maximum advantages of the invention will be obtained by the use of emulsions in which the liquefied gas is, or is contained, in the dispersoid, i. e. in the dispersed phase, and the liquid to be sprayed is the dispersant, i. e. the continuous phase. In other instances, it may be found advisable to have the liquefied gas as the continuous phase, or contained therein.

In spraying the emulsions of the present invention, they are maintained in a suitable spraying container under pressure created by the gasification of a portion of the liquefied gas of the emul-

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sion and the escape of such portion of the liquefied gas from the emulsion to the space within the spraying container above the emulsion. Liquefied gases are used which, when equilibrium is reached within the container during various stages of the spraying, will create a pressure above the emulsion sufficiently high to expel it with the desired force, and sufficiently high that when the emulsion is projected into the atmosphere, the pressure drop will be such as to cause substantially instantaneous boiling of the liquefied gaseous constituent of the emulsion. Such substantially instantaneous boiling of the gaseous constituent greatly facilitates the fine atomization of the liquid being sprayed, particularly if the liquid gas constituent is, or is in, the dispersed phase. In such cases, the instantaneous boiling of the liquefied gas within each sprayed droplet of the emulsion disrupts the droplet from within, almost with an explosive force, breaking it up into a myriad of still smaller droplets with the resultant formation of a very fine mist.

The invention is of broad scope as far as the nature of the liquid gaseous constituent and the liquid to be sprayed are concerned. The constituents of the emulsions of the present invention may be water-soluble, oil-soluble or soluble both in water and oil. Oil-soluble hydrocarbons such as propane or butane, or the halogen derivatives of methane and ethane, after being liquefied may be emulsified directly with a water phase, or they may be dissolved in an oil phase and the resulting solution emulsified with a water phase; or, if desired, they may first be emulsified in a water phase and the resulting emulsion subsequently emulsified in a continuous oil phase. However, generally the latter procedure is satisfactory only where the attendant increase in the viscosity of the final emulsion is not objectionable. Likewise, water-soluble gases, such as carbon dioxide and dimethyl ether, after being liquefied, may be emulsified directly with an oil phase, or they may be dissolved directly in a water phase and the resulting solution emulsified with an oil phase, or an emulsion first may be formed of such liquefied gases in a continuous oil phase and the resulting emulsion emulsified with a continuous water phase. In some instances, it is desirable to form emulsions in which a liquefied gas is contained both in the continuous and in the dispersed phases. For example, the same or different liquefied gases may be dissolved in two immiscible liquids, such as polar and non-polar liquids, and the two liquids containing the dissolved gases then emulsified; or the same or different liquefied gases

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may be formed into two immiscible emulsions and the two emulsions then mixed or emulsified one with the other.

As examples of gases which may be liquefied and used as the liquefied gaseous constituent of the emulsions of the present invention, the following are given:

Gas	Formula	B. P. (° C. atm. pr.)
Nitrogen	N <sub>2</sub>	-196
Methane	CH <sub>4</sub>	-161
Ethylene	C <sub>2</sub> H <sub>4</sub>	-104
Chlorine Fluoride	ClF	-101
Acetylene	C <sub>2</sub> H <sub>2</sub>	-88
Ethane	C <sub>2</sub> H <sub>6</sub>	-88
Carbon Dioxide	CO <sub>2</sub>	-78
Methyl Fluoride	CH <sub>3</sub> F	-78
Trifluoromethane	CHF <sub>3</sub>	-70
Hydrogen Sulphide	H <sub>2</sub> S	-62
Ketene	CH <sub>2</sub> CO	-56
Carbon Oxysulphide	COS	-48
Propylene	C <sub>3</sub> H <sub>6</sub>	-47
Propane	C <sub>3</sub> H <sub>8</sub>	-43
Monochlorodifluoromethane	CHClF <sub>2</sub>	-40
Cyclopropane	C <sub>3</sub> H <sub>6</sub>	-34
Chlorine	Cl <sub>2</sub>	-34
Trimethylene	C <sub>3</sub> H <sub>6</sub>	-34
Ammonia	NH <sub>3</sub>	-33
Chloro-Acetylene	C <sub>2</sub> HCl	-32
Monofluoroethane	C <sub>2</sub> H <sub>5</sub> F	-32
Propadiene	C <sub>3</sub> H <sub>4</sub>	-32
Dichlorodifluoromethane	CCl <sub>2</sub> F <sub>2</sub>	-30
Difluoroethane	C <sub>2</sub> H <sub>4</sub> F <sub>2</sub>	-30
Difluoropropylene	C <sub>3</sub> H <sub>3</sub> F <sub>2</sub>	-29
Hexafluoropropylene	C <sub>3</sub> F <sub>6</sub>	-29
Tetrafluoropropylene	C <sub>3</sub> H <sub>2</sub> F <sub>4</sub>	-28
Trifluoroethane	C <sub>2</sub> H <sub>3</sub> F <sub>3</sub>	-25
Dimethyl-Ether	C <sub>2</sub> H <sub>6</sub> O	-25
Diazomethane	CH <sub>2</sub> N <sub>2</sub>	-23
Allylene	C <sub>3</sub> H <sub>4</sub>	-23
Methyl Chloride	CH <sub>3</sub> Cl	-23
Propyne	C <sub>3</sub> H <sub>4</sub>	-23
Pentafluoropropylene	C <sub>3</sub> H <sub>2</sub> F <sub>5</sub>	-21
Formaldehyde	CH <sub>2</sub> O	-21
Trimethylboron	C <sub>3</sub> H <sub>7</sub> B	-20
Tetrafluoroethane	C <sub>2</sub> H <sub>2</sub> F <sub>4</sub>	-20
Pentafluoroethane	C <sub>2</sub> H <sub>3</sub> F <sub>5</sub>	-15
Tetrafluoromethane	CF <sub>4</sub>	-15
Vinyl Chloride	C <sub>2</sub> H <sub>3</sub> Cl	-15
Hexafluoroethane	C <sub>2</sub> F <sub>6</sub>	-10
Isobutane	C <sub>4</sub> H <sub>10</sub>	-10
Methylamine	CH <sub>3</sub> N	-7
Butylene	C <sub>4</sub> H <sub>8</sub>	-6
Butadiene	C <sub>4</sub> H <sub>6</sub>	-5
Monochloropentafluoroethane	C <sub>2</sub> ClF <sub>5</sub>	-5
Butane	C <sub>4</sub> H <sub>10</sub>	-2
Monochloroheptafluoropropane	C <sub>3</sub> ClF <sub>7</sub>	-2
Hexafluoropropane	C <sub>3</sub> H <sub>2</sub> F <sub>6</sub>	+2
Propylsulfide	CH <sub>3</sub> As	+2
Methylarsine	C <sub>2</sub> H <sub>5</sub> N	+3
Trimethylamine	C <sub>3</sub> H <sub>7</sub> N	+4
Dichlorotetrafluoroethane	CH <sub>2</sub> Br	+5
Methyl Bromide	C <sub>2</sub> H <sub>5</sub> Br	+5
Methyltrimethylene	C <sub>3</sub> H <sub>7</sub> N	+7
Dimethylamine	C <sub>2</sub> H <sub>5</sub> O	+7
Methyl-Ethyl Ether	CH <sub>3</sub> S	+8
Methylsulfide	C <sub>2</sub> ClF <sub>3</sub>	+8
Monochloropentafluoropropylene	C <sub>2</sub> H <sub>2</sub> O	+10
Ethyleneoxide	C <sub>2</sub> H <sub>3</sub> Cl	+12
Ethyl Chloride	C <sub>2</sub> H <sub>5</sub>	+10
Diacetylene	C <sub>2</sub> ClF <sub>2</sub> H <sub>2</sub>	+12
Monochlorotrifluoropropylene	C <sub>2</sub> H <sub>3</sub> N	+16
Ethylamine		

In some instances it is desirable to use a combination of two or more of the liquefied gases in order to impart to the resulting emulsion desired properties with respect to stability, vapor-pressure, self-propellancy, and ease of atomization when discharged through a restricted orifice.

The particular propellant gas which will be used will depend upon the nature of the liquid with which it is to be emulsified and various other factors such as the manner and place of use, toxicity, desired results, etc. It is, of course, important that in every instance the liquefied gas must be immiscible, relatively immiscible with, or soluble to a limited extent only in the liquid with which it is directly in contact, so that a true emulsion is formed. As examples of liquids to be sprayed which may be emulsified with the above liquefied gases there may be mentioned, as examples, insecticides, fungicides, parasiticides,

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fumigants, deodorants, perfumes, liquid waxes or wax solutions, cellulose derivative compounds, paints, lacquers, detergents, rust-preventive oils, impregnating compounds, lubricants, polishes, fire extinguishing compounds, dyes, rubber solutions, oils, etc.

When the liquid with which the liquefied gas is emulsified is a paint, lacquer, oil, liquid wax, or other coating composition, not only is the use of brushes or other applicators normally used for applying such compounds entirely eliminated but the coating may be applied much more rapidly, with greater uniformity and with a saving in the amount of material necessary to obtain a desired coverage.

If desired, finely-divided solid particles such as finely-ground insecticides such as sulfur, pyrethrin, rotenoids, etc., pigments, and the like may be suspended in and dispersed throughout the emulsion. Thus, the present invention contemplates self-propellant emulsions containing dispersed solid particles.

The emulsions contemplated by the present invention may be produced in any of the known ways of forming emulsions, no claim being made herein to the method by which the emulsions are formed. Homogenizers, colloid mills and agitators are examples of satisfactory forms of apparatus which may be used in forming the emulsions, as with the use of such types of apparatus emulsions can be formed in which the size of the dispersed particles may be as small as one-half micron. Emulsions in which the size of the dispersed particles are from about one-half micron to 5 microns are preferred, although emulsions containing the dispersed phase in droplets of larger size may be used.

Ordinarily, the emulsifying process is carried out under pressure regardless of the type of apparatus which is used. Hence, the apparatus should be so designed as to be gas tight and sufficiently strong to withstand the pressure at which the process is carried out, which may be, and usually will be, greater than that at which the resultant emulsion is stored.

Any of the known emulsified agents which are compatible with the liquefied gas and the liquids being emulsified may be used, such, for examples, as alkali with metallic soaps, sulfated oils or alcohols, aliphatic or aromatic sulfonates, cation active agents, and hydrophobic and hydrophilic esters and ethers. From the standpoint of corrosion, I prefer to use non-ionic emulsifying agents such as, diethylene glycol monolaurate, sorbitan monooleate, modified sorbitan, laurates, polyalkylene ether alcohol, etc., or emulsifying agents which function at least under neutral conditions. When such emulsifying agents are used, the final emulsion is less corrosive and may be stored in and sprayed from containers of iron, which ordinarily are cheaper than containers made of other materials.

In some cases, it may be desirable to add corrosion inhibitors to the emulsion or to coat the inside of the sprayer container and other parts thereof with which the emulsion may come in contact with a suitable lacquer or other corrosion-resistant coating. Likewise, it may be desirable to add an anti-freeze compound to the emulsion, particularly if the sprayer container therefor is to be used in cold climates.

The specific emulsifying agent which is used will, in many cases, depend upon the particular liquefied gas and other liquids which are to be emulsified. However, as there is a noted tend-

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ency towards the formation of foam when emulsifying a liquid gas with another liquid, and as the formation of foam during the emulsifying process results in small gas bubbles being occluded in the final emulsion which decreases its self-propelling properties, an emulsifying agent preferably is selected which tends to suppress foam formation, or which of itself is not foam forming. Likewise, the emulsifying agent should not be used in excess of that necessary to form and stabilize the desired emulsion.

The use of self-propellant emulsions of the type contemplated by the present invention possess many advantages. When water, or an aqueous medium is used as the continuous phase, or otherwise, as a solvent constituent of the emulsion, the cost is considerably less than when other solvents for the material to be sprayed are used, and the emulsion possesses non-inflammability properties. With many substances to be sprayed, better wetting, spreading and adhesion of the sprayed substance may be obtained, and it is possible to obtain satisfactory spraying by using less toxic, or non-toxic substances and substances which do not possess objectionable odors. Coatings also may be applied satisfactorily to moist surfaces, even if the continuous phase or other constituents of the emulsion are not water soluble. Also, the viscosity of the emulsion can be adjusted readily so that satisfactory spraying can be obtained with compounds which otherwise would be difficult because of their viscosity characteristics.

The use of emulsions of the present invention also provide for greater flexibility in formulating compounds suitable for spraying. As an example, there may be mentioned high viscosity coating compounds such as waxes, paints, lacquers, enamels, etc., which normally have to be thinned with expensive, inflammable and toxic solvents, to bring them to a state of fluidity such that they may be applied by brushing, or spraying with compressed air sprayers.

The emulsions of the present invention also possess advantages over spraying compositions in which a liquefied gas and the substance being sprayed are formed into a solution, as where a high viscosity coating compound is dissolved in a liquefied gas. In such cases a greater amount of energy (more of the liquefied gas) must be used to break or atomize such compounds into a suitable spray after they leave the spray nozzle.

In accordance with the present invention, when highly viscous compounds, such as those mentioned above, are to be sprayed they may be formed into an oil-in-water emulsion, in which the water is the continuous phase. Consequently, the resulting emulsion possesses high fluidity, even when the viscous compound to be sprayed is at high concentration in the internal or dispersed phase of the emulsion. In such cases, the highly viscous nature of the internal or dispersed phase does not influence the fluidity of the emulsion so that the concentration of such viscous compounds consequently can be very high. Hence, it is possible to formulate emulsions of highly viscous coating compounds where practically the only thinner used is a liquefied gas which is in solution with or emulsified with the viscous coating compound in the dispersed phase of the emulsion. In the latter case, particularly if the liquefied gas is the continuous phase of the emulsion with the compound to be sprayed, the liquefied gas may be one having a relatively high boiling point but sufficiently low that on

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spraying of the emulsion the liquefied gas will quickly evaporate from the resulting atomized spray. It may be found desirable to use a propelling agent which is water soluble, such as, for example, dimethyl ether, as the water, on boiling and evaporation of the propelling agent from the sprayed droplets, will more readily and easily break up into a fine spray than the viscous coating compound which is contained in the dispersed phase of the emulsion being sprayed. In such cases the viscous compound to be sprayed can be emulsified with and form the dispersed phase of an emulsion with a solution of water and the water soluble propelling agent. However, it has been found that even with coating or spraying compounds of extremely high viscosity in the dispersed phase of the emulsion, the liquefied gases can be incorporated in them, either by solution or emulsification, and on spraying breaks up the water rather than the viscous compound contained in the internal or dispersed phase. That probably is due to surface evaporation from the emulsified particles, it being understood that the total surface of the emulsified particles in a finely atomized spray is enormously large.

Another advantage of using the emulsions of the present invention is the ease with which solid particles such as pigments, insecticides, etc. may be dispersed in them and prevented from settling out as they would from solutions of compounds to be sprayed in liquefied gases.

The emulsions contemplated herein lend themselves to phase-reversal of a controlled and desirable type. For example, the emulsion to be sprayed may be of the water-in-oil type as initially prepared and as maintained inside of the sprayer container so that the inside of the container and the portions thereof through which the emulsion passes during spraying will be in contact with the oil of the emulsion rather than the water thereof, in order that corrosion of the container and the parts thereof will not take place. That is particularly so when the oil is one having high fluidity, such as the oils used in perfumes, insecticides, etc. In such a case, the propelling agent or the liquefied gas may be propane or butane dissolved in the oil phase to such an extent that when it evaporates upon discharge from the container the volume of the external phase suddenly decreases and brings about an automatic reversal of phase, it is to be understood that the emulsifying agent and other factors correctly are selected. The reversal of phase results in an oil-in-water emulsion which has excellent penetrating and wetting power for water-wettable surfaces like paper, cardboard, wood, fabrics, etc. Also, as the water then is the continuous phase it readily may evaporate from about the dispersed particles of paint, etc., on a surface onto which the spray is directed. If such reversal in phase did not take place, the water, when the spray hits the surface to be coated, still would be in the dispersed phase, and consequently could not readily evaporate from the continuous phase of the paint etc.

Where corrosion is not a serious problem, the emulsion initially may be of the oil-in-water type and the water contain a liquefied gas, such as dimethyl ether, in solution. With the use of a suitable emulsifying agent and other conditions being suitable such emulsion on spraying will change phase due to evaporation of liquefied gas, producing a water-in-oil emulsion which more readily will penetrate and wet non-polar surfaces or surfaces which normally are not readily wetted

by water, such as rubber, oil, linoleum, metal, glass and the waxy skin of insects. The advantage of such phase reversal can readily be appreciated in cases where the oil or dispersed phase is of an extremely viscous character.

In like manner, reversible emulsions in which an initial oil-in-water emulsion is emulsified in a continuous oil phase, or an initial water-in-oil emulsion is emulsified in a continuous water phase can be prepared and caused to reverse upon spraying, if desired.

An important feature of the present emulsions is the addition of the water-phase to the compound to be sprayed, which in addition to the advantages which it offers to presently known emulsions, makes self-propellant emulsions non-inflammable even when using inflammable propelling agents and other materials. For example, the case where a paint is first emulsified in water to form an oil-in-water emulsion, which in turn is emulsified with an oil soluble liquefied gas as the continuous phase. When such a final emulsion is discharged from a sprayer, the atomized stream will consist of a gas carrying fine droplets of the initial emulsion of the paint emulsified in a continuous water phase. In such a case the high heat capacity of the droplets of paint emulsified in water will prevent the liquefied gas of the emulsion being sprayed from freezing the discharge nozzle and will render the gas stream practically non-inflammable due to the presence of the water particles and water vapor in the stream. On the other hand, the oil phase inside the water droplets will not evaporate during the spraying. Thus, any toxic fumes or vapors which the paint or other substance emulsified in the water normally might give off are avoided and an actual saving in the material to be sprayed obtained. On the contrary, when a binary solution of liquefied gas and oil or paint, such as heretofore have been proposed are sprayed, the evaporation of the gas causes a considerable portion of volatile components of the oil to evaporate so that an excess amount of such volatile components must be used in order to have enough left to obtain the necessary coverage, wetting action, spreading action, etc., when the material hits the surface or object to be coated.

Emulsions consisting of an initial emulsion of water in a continuous oil phase which subsequently are emulsified in a continuous water phase will behave substantially in the same manner as described above with respect to emulsions formed by first emulsifying a oil in a continuous water phase and then emulsifying that emulsion in a continuous oil phase. If, for example, liquefied hydrocarbon gases such as propane or butane are dissolved in an oil phase, a phase reversal can be made to take place when the liquefied gas evaporates so that droplets consisting of an oil-in-water emulsion are formed upon discharge of the emulsion from the sprayer. In such cases, some of the water will be present in the atomized spray as separate water particles of a much smaller size than the particles of the oil-in-water emulsion and will impart additional non-inflammable properties to the spray.

In order further to illustrate the scope of the present invention with respect to the formation of emulsions containing a liquefied gas for various purposes, reference is made to the examples set forth below. However, it is to be understood that the invention is not limited merely to such emulsions, or to the method of spraying such emulsions. In all of the examples the relative

amounts of the various components of the emulsions, whether expressed by per cent or by parts, are by weight, unless otherwise stated.

*Insecticide.*—A self-propellant emulsion for insecticidal purposes was prepared by adding 30% by volume of liquefied butane and 10% by volume of liquefied dimethyl ether to 60% by volume of water containing an active insecticide, such as dichloro diphenyl trichloro ethane (D. D. T.) Thanite, or pyrethum extract, with a small amount of emulsifying agent. The mixture thus prepared was agitated in a pressure vessel until the self-propellant emulsion was formed.

*Moth-proofing compound.*—A self-propellant emulsion for moth-proofing garments and other fabrics was prepared by melting 1.5 parts of diglycol stearate, as an emulsifier, into 60 parts of water at a temperature of 90° C. and then adding 5 parts of liquefied methyl chloride. A solution of 15 parts of paradichlorobenzene in 18.5 parts of liquefied butane was next prepared and slowly added to the water solution of methyl chloride and emulsifier, under constant stirring. The mixing was carried out in a pressure vessel to prevent evaporation and escape of the liquefied gases. The resulting emulsion was pumped into suitable spraying containers provided with nozzles for atomization of the emulsion when expelled. There was sufficient evaporation of the liquefied gases from the emulsion in the container to create an ample expelling pressure for the remainder of the emulsion. On opening the valve of the spray container, the vapor pressure expelled the emulsion, which, on escape from the nozzle, broke up into fine particles.

*Wax emulsion.*—A suitable self-propellant wax emulsion for spraying onto floors and other surfaces to be waxed can be prepared by first melting the desired waxes at elevated temperatures and dissolving them in suitable liquefied gases such as liquefied butane, propane or methyl chloride, under pressure. Water, triethanolamine, stearic acid and dimethyl ether, ethyl ether or ethylmethyl ether then are blended together and heated under pressure, with resultant formation of a soap solution. The wax solution then is slowly added, with agitation, and in a pressure vessel, to the soap solution, and the resulting emulsion is cooled slowly. A specific example of a self-propellant wax emulsion so formed may include the following ingredients in the stated proportions:

	Parts
Ceresin wax.....	20
Paraffin wax.....	20
Liquefied butane.....	20
Water.....	75
Liquefied dimethyl ether.....	15
Stearic acid.....	5
Triethanolamine.....	2.5

The esterification of the stearic acid with the triethanolamine results in the formation of a soap which acts as a suitable agent for the emulsification of the wax with the other constituents.

*Lacquer emulsion.*—A suitable self-propellant lacquer emulsion may be prepared by first preparing a solution of:

	Per cent
Nitrocellulose.....	30
Butyl acetate.....	20
Butyl alcohol.....	10
Castor oil.....	25
Liquefied dichlorodifluoromethane.....	15

The above ingredients are mixed together in a suitable pressure vessel, in order to prevent the evaporation and escape of the dichlorodifluoromethane. Next, there is prepared a mixture of:

	Per cent
Duponol .....	1
Sulfated castor oil .....	2
Liquefied dimethyl ether .....	40
Water .....	57

The latter constituents are mixed together in a separate vessel, under pressure, and then added to the first-prepared lacquer solution, after which the resulting mixture is passed through a colloid mill to obtain a fine particle-size emulsion which may be sprayed from suitable spray containers as described above.

**Dry-cleaning soap emulsion.**—A satisfactory self-propellant dry-cleaning soap emulsion was prepared by esterifying 6% of oleic acid with 3% of triethanolamine to form a triethanolamine soap. 10% of carbon tetrachloride and 46% of solvent naphtha were then separately mixed with 35% of liquefied dichlorodifluoromethane and the resulting mixture added, under constant agitation, in a pressure vessel, to the triethanolamine soap. The agitation was continued until a suitable emulsion was formed. The emulsion was self-propellant and practically non-inflammable.

**Impregnating compound.**—A suitable self-propellant impregnating compound was prepared by mixing, under pressure, and then passing through a colloid mill to secure a uniform emulsion, the following constituents in the amounts indicated:

	Per cent
Creosote .....	35
Potassium dichromate .....	5
Sodium fluoride .....	20
Dinitrophenyl .....	2
Bentonite .....	8
Water .....	15
Liquefied butane .....	10
Liquefied methyl chloride .....	5

**Oil emulsion.**—A self-propellant emulsion suitable for dressing leather was prepared from the following constituents:

	Per cent
Neat's-foot oil .....	40
Water .....	40
Oleic acid .....	5
Triethanolamine .....	1
Liquefied monochlorodifluoromethane .....	5
Liquefied butane .....	9

Part of the oil, the oleic acid, triethanolamine and the liquefied gases were first mixed together, under pressure, after which part of the water was added, with stirring, and under pressure. Thereafter, and while still under pressure, the remainder of the oil was added, and finally the remainder of the water, such addition of the remainder of the oil and the water being with constant agitation. The ingredients were agitated until a satisfactorily uniform emulsion was obtained. The resulting emulsion, on spraying, was found to give a finely atomized mixture, well suited for the treating of leather and similar goods.

**Adhesives.**—A self-propellant adhesive emulsion containing rubber latex as the essential adhesive agent was prepared with the following constituents:

	Per cent
Latex solution (containing 40% latex) .....	50
Neutral ammonium sulfuricinate .....	0.5
Liquefied dimethyl ether .....	10
Liquefied butane .....	10
Liquefied dichlorodifluoromethane .....	5
Toluene .....	24.5

The latex, ammonium sulfuricinate, and the liquefied dimethyl ether first were carefully mixed, under pressure. The liquefied butane, the liquefied dichlorodifluoromethane and the toluene were then separately mixed and added to the mixture of latex, ammonium sulfuricinate and dimethyl ether. The mixing was conducted in a pressure vessel, with stirring, and the final mixture agitated until a uniform emulsion suitable for use in spray containers was obtained.

**Drying-oil emulsion.**—A satisfactory self-propellant drying-oil emulsion was prepared from the following constituents:

	Per cent
Linseed oil .....	40
Oleic acid .....	5
Triethanolamine .....	1
Liquefied butane .....	10
Liquefied propane .....	4
Water .....	40

The triethanolamine, oleic acid, the liquefied butane and part of the linseed oil first were mixed together to form a homogeneous mixture, after which part of the water was slowly added, with stirring, to form an emulsion. After that, the remainder of the oil and the liquefied propane were added, with agitation, and finally the remainder of the water was added while the previously-formed emulsion was being agitated. The resulting emulsion was then passed through a homogenizer for the purpose of securing fine particle-size of the emulsion and to obtain a good, stable emulsion satisfactory for use in spray containers.

**Deodorizing emulsion.**—A self-propellant deodorizing emulsion was prepared from the following constituents:

	Per cent
Pine oil .....	35
Liquefied propane .....	18
Oleic acid .....	5
Triethanolamine .....	2
Water .....	35
Liquefied dimethyl ether .....	5

The oleic acid, triethanolamine, about one-third of the pine oil and the liquefied propane were mixed together and agitated, under pressure, after which a part of the water was added, with stirring, with resultant formation of an emulsion. To the emulsion thus formed the remainder of the pine oil and the liquefied propane were added with vigorous stirring, and finally the remainder of the water and the dimethyl ether added. The resulting emulsion was passed through a colloid mill and then filtered and pumped into suitable spray containers.

**Asphalt emulsion.**—A self-propellant asphalt emulsion suitable for spraying was prepared, using the following constituents:

	Per cent
Asphalt .....	60
Duponol .....	2
Liquefied butane .....	10
Liquefied propane .....	5
Liquefied dimethyl ether .....	3
Water .....	20

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The asphalt was first heated and mixed with the liquefied propane and the liquefied butane, under pressure. The water, methyl ether and Duponol were then mixed together and vigorously agitated, while being heated. The latter mixture was then added to the mixture of asphalt, liquefied butane and liquefied propane and passed through a suitable homogenizing apparatus to form a fine emulsion, suitable for spraying from spray containers.

*Road-spraying emulsion.*—A self-propellant emulsion suitable for road-spraying and containing tar oil as a base was prepared, using the following constituents:

	Per cent
Tar oil .....	60
Liquefied butane .....	15
Duponol .....	5
Calcium chloride .....	2
Sodium bichromate .....	1
Liquefied dimethyl ether .....	7
Water .....	10

The Duponol, an emulsifying agent, was added to a warm mixture of the tar oil and liquefied butane. The calcium chloride, the sodium bichromate and the dimethyl ether were then mixed with the water to form an aqueous solution which was added to the solution of the tar oil in the liquefied butane. The mixture was suitably agitated, under pressure, until a satisfactorily-uniform emulsion was prepared, suitable for the spraying onto roads to keep down dust.

*Ski-wax emulsion.*—A satisfactory self-propellant wax emulsion for treating ski was prepared from the following constituents:

	Per cent
Beeswax .....	10
Ozokerite .....	10
Paraffin wax .....	10
Rosin .....	10
Morpholine .....	5
Oleic acid .....	5
Dimethyl ether .....	15
Water .....	35

The waxes and rosin were melted together and then mixed with the oleic acid and the dimethyl ether, under pressure. The resulting mixture was permitted to cool slowly, after which the morpholine and the water were added with vigorous agitation until a fine uniform emulsion was formed. The self-propellant emulsion thus formed was satisfactory for spraying from spray containers and has the advantage that it may satisfactorily be sprayed onto ski even though the surface onto which the emulsion is to be sprayed is not dry.

From the foregoing it will be seen that the present invention provides a new type of self-propellant composition and a method of spraying the same which is adapted to the spraying of various types of compositions for various purposes.

I claim:

1. The method of spraying which comprises

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initially forming an emulsion comprising two immiscible liquids in emulsified form, said emulsion having water in the continuous phase and a liquefied gas in the dispersed phase, maintaining the emulsion in a hermetically-sealed container under pressure formed by vaporization of a portion of the liquefied gas from the emulsion, and expelling the emulsion under such pressure through a restricted orifice.

2. The method of spraying which comprises initially forming an emulsion comprising two immiscible liquids in emulsified form, the dispersed liquid comprising a solution of two liquids, one of which is a liquefied gas, maintaining the emulsion in a hermetically-sealed container under pressure formed by vaporization of a portion of the liquefied gas from the emulsion, and expelling the emulsion under such pressure through a restricted orifice.

3. The method of spraying which comprises initially forming an emulsion comprising two immiscible liquids in emulsified form, the dispersed liquid comprising a liquefied gas, maintaining the emulsion in a hermetically-sealed container under pressure formed by the vaporization of a portion of the liquefied gas from the emulsion, and expelling the emulsion under such pressure through a restricted orifice.

4. A package comprising a hermetically-sealed container charged, under pressure, with an emulsion comprising two immiscible liquids in emulsified form, said emulsion having a liquefied gas in the dispersed phase, and a propellant gas under pressure sufficient to propel the emulsion from the container.

5. A package as set forth in claim 4 in which the liquefied gas is a hydrocarbon.

6. A package as set forth in claim 4 in which the liquefied gas is a halogenated hydrocarbon.

7. A package as set forth in claim 4 in which the liquefied gas is an ether.

8. A package as set forth in claim 4 in which the continuous phase of the emulsion includes water.

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