

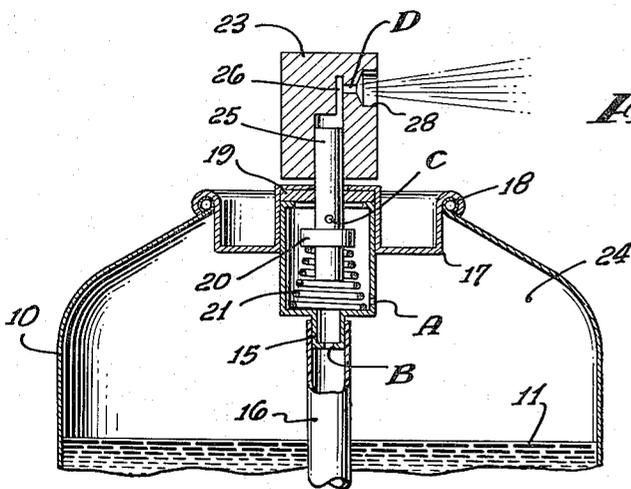
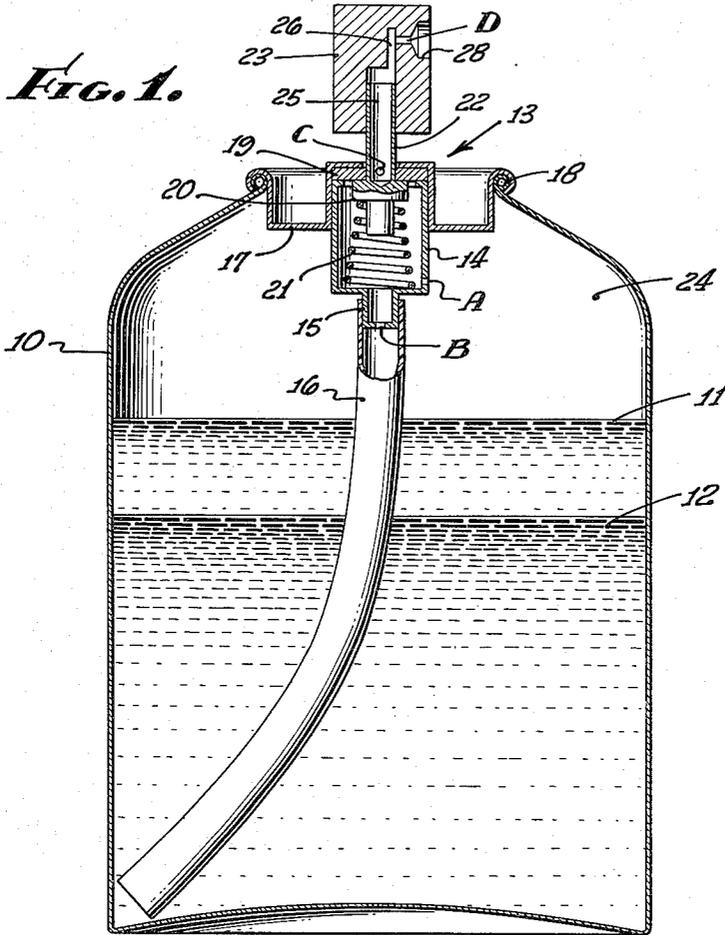
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2,995,278

PACKAGED SELF-PROPELLING LIQUID COMPOSITIONS

Filed May 22, 1959



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2,995,278
PACKAGED SELF-PROPELLING LIQUID
COMPOSITIONS

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6 Claims. (Cl. 222—394)

This invention relates to hermetically sealed packages of self-propelling pressure liquid compositions equipped with specially designed valving mechanisms from which application is made in the form of a non-foaming or low-foaming atomized spray. More particularly, this invention relates to alcohol-containing water solutions of various substances which are propelled through specially designed valving mechanism by insoluble, liquefied propellant mixtures to dispense such substances finely atomized in non-flammable sprays. The invention has particular, though typical, applicability to improved "sprays" for filming the hair to beautify and hold it in place and to facilitate various hair stylings.

Heretofore in the hair styling field of such self-propelling pressure liquid products, anhydrous systems employed commercially have consisted essentially of anhydrous liquid compositions containing in solution alcohol, chlorinated hydrocarbon propellants such as dichlorodifluoromethane or dichlorotetrafluoroethane, in combination with hydrolyzable trichloromonofluoromethane or dichloromethane or methyl chloroform, and shellacs or resins such as polyvinylpyrrolidone, or its vinyl acetate copolymers, along with plasticizers and suitable perfumes. Because trichloromonofluoromethane, dichloromethane and methyl chloroform have high hydrolysis rates and form with moisture, corrosive chloride compounds which attack metal containers, it has been necessary to keep the level of moisture very low (below 0.1%) and thereby preclude the use of water soluble resins.

It has been proposed to utilize aqueous systems for the purpose of dispensing colognes and the like, where the propellant is immiscible with and heavier than the aqueous phase, but this has several inherent disadvantages; one being that a promoter for vaporization of the propellant is required, and another that the eductor tube must be shortened to keep from expelling the liquid propellant, which results in incomplete dispensing of the product. Also, the spray so produced is not sufficiently atomized, because propellant vapor is not introduced into the material while it is being ejected. If this were done, additional quantities of propellant would be required with an additional shortening of the tube and lack of complete emptying of the container.

It has also been proposed to dispense water-containing products from liquefied propellant-aqueous emulsion systems, but this results in the production of a foamy spray, which in the case of hair sprays, leaves an initially undesirable deposit on the hair. Also, water based products have been dispensed by using small percentages of flammable hydrocarbons where the hydrocarbon floats on top of the liquid and remains behind in the container to eliminate the flammability factor. Again, limited atomization of the spray is encountered since there is no mixing of the vapor with the liquid being dispensed, and only small amounts of propellant can be used to prevent highly flammable liquid from being dispensed when the container becomes nearly empty.

The present invention overcomes these various objections and limitations by employment of aqueous systems containing propellant mixtures, the specific gravity of which may be adjusted close enough to that of the

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aqueous phase to be easily mixed with the latter by simple agitation if it is desired to have liquid propellant expelled along with the aqueous phase and propellant vapor. Being lighter, the propellant mixture will not settle out on the bottom of the container. By forming the propellant mixture of a chlorinated propellant plus hydrocarbon propellant, with the vapor pressure of the chlorinated fraction equal to or greater than that of the hydrocarbon, as vapor is bled away the specific gravity of the propellant phase will tend to decrease.

The invention is predicated upon the use, in addition to the fluid contents of the package, of a valving device associated with the pressure container and including a mixing chamber and communicating orifices, in such relation as to receive, mix and dispense the package contents in a manner assuring the formation of a highly effective spray which, notwithstanding the flammable propellant component, is itself non-flammable according to the standard tests. Briefly, the valve device comprises a mixing chamber connected through separate orifices with the liquid and vapor phases in the container, and a valve proper which controls release of fluid from the mixing chamber through a discharge passage to the spray orifice. Using this type of mixing and valve arrangement, and by control of orifice sizes, it is possible to achieve a pre-mixing of the liquid and gaseous phases from the container that will result in release of the aqueous phase, or mixed aqueous and non-aqueous phases, in a finely atomized non-flammable spray.

At this point it may be mentioned that spray flammability is regarded in reference to standard tests, according to one of which flammability is determined by measuring projection of the flame of a burning taper placed at a distance of 6 inches from the dispenser valve while spraying through the flame. To be considered completely non-flammable the flame must be projected less than 8 inches from its source. Another test is to spray for one minute into an opened and then closed 55 gallon drum in which is placed a burning taper. There must be no flame propagation in the open drum or explosion in the closed drum.

Water is used together with either or both ethyl alcohol or isopropyl alcohol in the formulations contemplated by the invention in order to inhibit flammability where desired, to reduce the ingredient cost, and to make possible the use not only of organic additives such as resins, that are soluble in anhydrous alcohol and propellant mixtures, but those which are soluble in water and alcohol mixtures as well. As previously indicated, the inability to use water has been a great handicap in the past since there have been few resins available commercially that have the solubility and film forming characteristics necessary for such purposes as hair sprays.

The following are illustrative organic materials in the category of natural and synthetic resins, the use of which are now made possible by the present invention: Water-alcohol soluble cellulose and derivatives such as methyl cellulose, sodium carboxymethyl cellulose, hydroxyethyl-cellulose and its carboxymethyl copolymers; water-alcohol soluble starch derivatives such as starch acetates, ethers and esters (some of these may require special processing such as cooking to attain proper solutions and films); water-alcohol soluble amino acid-type polymers such as zein and casein (some of these perform best in mildly alkaline solutions); water-alcohol soluble polyacrylates such as sodium polyacrylate; water-alcohol soluble carbohydrate polymers such as "Polyose" manufactured by Corn Products Refining Company; water-alcohol soluble low toxic synthetic polymers such as "Ciba Resin #325"; water-soluble vinyl polymers such as polyvinyl alcohol, polyvinyl pyrrolidone and the vinyl acetate

copolymers, polyvinylethers and their esters, polyvinyl formal, and polyacrylamides.

Most of the above-mentioned resins may require plasticization to render the films sufficiently flexible to prevent undesirable flaking on the hair. Examples of plasticizers that may be employed are: glycols, such as propylene, triethylene dipropylene, etc.; glycerine, glycerol ethers and esters; sorbitols; polyethylene glycols and suitable ether and ester derivatives thereof; polyoxethylenes and their suitable ether and ester derivatives; and polyethylene oxide condensates.

The problem of hydrolysis of the halogen substituted propellant is eliminated by using one or a mixture of those propellants having very low rates of hydrolysis. Examples of these are dichlorodifluoromethane, dichlorotetrafluoroethane, octofluorocyclobutane, monochlorodifluoromethane, and monochlorotrifluoromethane. Hydrocarbon propellants to be used with the halogen-substituted propellant include propane, isobutane, N-butane, 2,2-dimethyl propane, and isopentane. Of these N-butane (or isobutane) is preferred because of its availability and suitable vapor pressure.

Mixtures of halogen-substituted and hydrocarbon propellants may be determined generally as follows: The specific gravity of the water based phase is determined at 68° F. Next the absolute vapor pressure and liquid densities of the propellant constituents are recorded from existing literature. The mole fraction of each propellant constituent of the selected blend is multiplied by its liquid density and added together. The total should not exceed the density of the aqueous phase by more than about 0.01 gm. per cc. and should be adjusted close to the aqueous phase where large percentages of propellant will be employed. The same method is applied to vapor pressure to determine roughly what the vapor pressure of the mixture will be. Next, the vapor pressures of the chlorinated constituents should be equal or exceed that of the hydrocarbon constituents to insure equal or more rapid removal of the chlorinated hydrocarbon from the vapor phase so that density changes of the propellant mixture will remain the same or become lower.

The water-alcohol ratio should normally be established between about 10 percent alcohol and 90% water, to about 70% alcohol and 30% water. Factors to be considered in establishing this ratio are: Flammability considerations, i.e., whether or not it is necessary to have a completely non-flammable spray or if some flammability is permissible; resin solubility, in that some resins will tend to become insoluble at different concentrations of water-alcohol which will result in valve clogging. The propellants employed are very insoluble in water, and consequently one would be required to have less than about 30% water to 70% alcohol at a propellant concentration less than about 15% to form miscible systems. Rate of drying may be adjusted somewhat by the degree of atomization but the quantity of alcohol present will influence the speed of drying. With all constituents of the formula held constant except the water-alcohol ratio, increasing the alcohol will speed up drying time of the applied material. It may be mentioned at this point that the quantity of propellant employed will also affect the drying time when the dispenser is agitated prior to spraying.

Another advantage of the invention is that fairly wide variations of propellant to aqueous phase may be used when the densities of the two phases are adjusted close together and/or the viscosity of one of the phases, preferably the aqueous phase, is increased. In this manner, the two phases which normally or in static condition are essentially unmixed, i.e. individually continuous phases, are easily mixed with moderate agitation and remain interspersed for a considerable time. The ratio of propellant phase to aqueous (active ingredient) phase may be varied from about 15% (by weight) to about 70% of the aqueous phase. At the higher propellant

ratios, sprays may be obtained without the vapor phase orifice, but higher degrees of flammability are encountered. Physical mixing is necessary at high propellant concentrations for uniform container emptying.

Films for the hair may be colored or tinted by incorporating small amounts of water-alcohol soluble dyes in the aqueous phase. These dyes are useful for highlighting the hair and covering gray hair where desired.

The invention will be further understood by reference to the accompanying drawing, in which:

FIG. 1 is a view showing in vertical section a pressure container in which the aqueous and propellant phases appear, and having a top mixing and dispensing valve assembly of the type previously mentioned; and

FIG. 2 illustrates the spray dispensing valve in open position.

The package is shown to comprise a container 10 for the upper non-aqueous liquid phase 11 and the lower aqueous phase 12, the character and compositions of which have been referred to hereinabove. The top of the container carries a dispensing valve assembly generally indicated at 13 and comprising a main or initial mixing chamber 14, the bottom reduced end 15 of which is joined to an eduction tube 16 extending to the bottom of the container. Chamber 14 is fixed within a head 17 crimped at 18 to the wall of the container, the chamber being engaged and retained upwardly against a seal ring 19.

The valve proper indicated at 20 seats upwardly against the ring 19 under the influence of spring 21, and has a tubular stem 22 carrying a head 23 which when pressed downwardly against the resistance of the spring opens the discharge ports and passages to release the aqueous phase in atomized spray pattern. Vapor space 24 in the container communicates with the mixing chamber through a restricted orifice A, and upon opening of the valve, the vapor pressure in the container displaces fluid upwardly through the tube 16 into the mixing chamber through a second orifice B within the tube. The effect of the combined gas and liquid introduction to the mixing chamber respectively through orifices A and B is to produce within the chamber a preliminary mixing of the liquid and gaseous phases in such intimacy as will contribute ultimately to the desired formation of a spray in which the liquid is dispersed in very fine particles enveloped within the expelled gas. When the valve is open to the FIG. 2 position, the pre-mixed gas and liquid are discharged through orifice C into a secondary mixing chamber 25 within the stem 22, from which the mixture is discharged in spray form through a mechanical break-up type of outlet formed by passage 26 and a fourth orifice D within the counterbored mouth 28.

The size of orifice B which controls flow of liquid active ingredients should be about equal to gas orifice A or somewhat larger. The ratio of these orifices will be governed to some degree by orifices C and D. Vapor orifice A should be about equal to or greater than liquid orifice B for sufficient atomization effect, and its size may be governed to some extent by orifices C and D. Orifice C should be equal to or greater than orifice A to allow sufficient pressure drop in chamber 14 that liquid will be forced through orifice B to be expelled from said container. Orifice D should also be equal to or greater than orifice A to allow sufficient pressure drop in chamber 14 that liquid will be forced through orifice B to be expelled from said container. The ratio of orifice D to C, or vice versa, is not greatly critical so long as their ratio to orifice A is maintained. Expansion chamber 25 should be of minimum size to prevent spitting of spray when valve is closed off after spraying, since liquid-vapor mixture remaining in the chamber loses its vaporizing action when orifice C is closed suddenly. When the chamber size is below 0.2 cc., the spitting is only slight and is nearly eliminated by reducing volume of chamber 25 still further.

Concerning usable orifice size ranges and ratios (expressed as diameters), the size of orifice A should be between about 0.008 in. to 0.018 in., and assuming orifice A size as unity in ratio expressions: the size of orifice B will be from about 0.0075 to 0.026 in., with the ratio of A to B, to be about 0.9 to 3.0; the size of orifice C, which is not critical on the large size, may range between about 0.010 and 0.11 in., with the ratio of A to C between about 1.2 to 6.0; and the size of orifice D may be between about 0.008 to 0.026 in., and the ratio of A to D about 1.0 to 3.0.

Referring back to the aqueous and non-aqueous phase contents of the package, their composition relations and ranges are as follows: The bottom aqueous phase 12, ranging from about 30 to 80 percent of the total liquid (both phases), will contain about 10 to 70 percent alcohol and typically about 1.0 to 10 percent organic additive in the class of resins, plasticizers, perfumes, insecticides etc., depending upon the particular product. The non-aqueous phase 11 will comprise between about 30 and 70 percent hydrocarbon and a corresponding range of the liquefied halogen substituted propellant. The ratio of the specific gravity of the non-aqueous phase to the aqueous phase will be between about .990 to 1.000 and 1.010 to 1.000. The ratio of the vapor pressure of the halogen-substituted propellant to the vapor pressure of the hydrocarbon falls in the range of about 4 to 1 and 1 to 1, with their combined vapor pressures being usually in the range of about 25 to 70 p.s.i.g. at 70° F. In the case of compositions such as hair sprays, containing water soluble resins and plasticizers, the resin content ordinarily will be between about 1 to 8 percent by weight of the aqueous phase weight, with the required plasticizer ordinarily being less than the resin.

The following may be cited as typical base compositions (and orifice sizes), which may be supplemented with suitable organic additives to make products in various categories:

Example I

Dichlorodifluoromethane -----	Percent	
n-Butane (commercially pure)-----	30	} 20
Water -----	70	
Alcohol -----	60	} 80
	40	

Valve orifice diameters: orifice A, .013"; orifice B, .018"; orifice C, .040"; orifice D, .016-.018", with mechanical breakup design. Specific gravity of propellant mix is about 0.71 at 60° F., vapor pressure about 33-35 p.s.i.g. at 70° F.

Example II

Dichlorodifluoromethane -----	Percent	
n-Butane -----	50	} 50
Water -----	50	
Alcohol -----	40	} 50
	60	

Valve orifice diameters: orifice A, .013"; orifice B, .013"; orifice C, .040"; orifice D, .016-.018". Specific gravity of propellant blend is about 0.82 to 60° F., vapor pressure about 41 p.s.i.g. at 70° F.

Example III

Dichlorodifluoromethane -----	Percent	
n-Butane -----	57.6	} 40
Water -----	42.4	
Alcohol -----	30.0	} 60
	70.0	

Valve orifice diameters: orifice A, .013"; orifice B, .013"; orifice C, .040"; orifice D, .018". Specific gravity propellant blend is about 0.87 at 60° F., vapor pressure about 45 p.s.i.g. at 70° F. Above example forms an excellent dispersion,

Example IV

Dichlorodifluoromethane -----	Percent	
n-Butane -----	45	} 30-30
Dichlorotetrafluoromethane -----	25	
Water -----	90	} 70
Alcohol -----	10	

Valve orifice diameters: orifice A, .013"; orifice B, .018"; orifice C, .040"; orifice D, .016". Specific gravity of propellant blend about .98 at 60° F., vapor pressure about 37 p.s.i.g. at 70° F.

The following are illustrative compositions formulated for the particular uses indicated:

Example V

Room deodorant formulation:	Percent
Solubilized perfume-----	1.0
Ethyl alcohol-----	36.0
Distilled water-----	30.0
Triethylene glycol-----	3.0
n-Butane -----	15.0
Dichlorodifluoromethane -----	15.0

Valve—orifice B, .013"; A, .013"—.014"; C, .025-.030"; D, .018", mechanical breakup.

Example VI

Hair spray formulation:	Percent
Methyl cellulose-----	1.5
Propylene glycol-----	0.15
Solubilized perfume-----	0.15
Ethyl alcohol-----	25.0
Distilled water-----	38.20
n-Butane -----	12.5
Dichlorotetrafluoroethane -----	2.5
Dichlorodifluoromethane -----	10.0

Valve—orifice B, .013"; A, .013"; C, .020"—.030"; D, .016-.020".

Example VII

Cologne spray:	Percent
Solubilized perfume-----	1.5
Ethyl alcohol-----	40.0
Distilled water-----	31.5
n-Butane -----	14.0
Dichlorotetrafluoroethane -----	3.0
Dichlorodifluoromethane -----	10.0

Valve—orifice B, .013"; A, .013"; C, .020"; D, .020".

Example VIII

Insecticide spray:	Percent
Pyrethrins -----	0.5
Piperonyl butoxide-----	2.0
Sorbitan monooleate-----	1.0
Deodorized kerosene-----	3.0
Ethyl alcohol-----	38.0
Water -----	15.0
Dichlorodifluoromethane -----	23.0
n-Butane -----	17.5

Valve—orifice B, .011"; A, .013"; C, .030"; D, .018", mechanical breakup.

All of the above examples will yield well atomized sprays. Examples V and VIII are well into the true aerosol particle range (less than 50 microns), whereas Examples VI and VIII are wetter because the application is to be on a surface. All of the esprays are no-flammable when tested as described.

As will be understood, the invention contemplates that products formulated in accordance therewith may contain dispersed solid particles. Thus in products such as insecticides, one of the active components may be in powder form.

I claim:

1. A package, comprising a pressure container, a pressurized gas phase in the upper interior of the container, a liquid composition in the container below said gas phase, said liquid composition consisting essentially of between about 35 and 80 percent of a liquid aqueous phase and the balance a liquid non-aqueous phase, said phases in static condition being essentially separate from each other and the specific gravity of the liquid non-aqueous phase being less than that of the liquid aqueous phase so that the static liquid non-aqueous phase remains on top of the liquid aqueous phase but is miscible therewith by agitation if desired, said liquid aqueous phase comprising an organic solute dissolved in a solution of about 30 to 90 percent water and about 70 to 10 percent alcohol of the group consisting of ethyl alcohol and isopropyl alcohol, said liquid non-aqueous phase being normally gaseous and containing flammable hydrocarbon, said gas phase comprising vapor from said liquid non-aqueous phase, and a dispensing assembly carried by the container and including a mixing chamber having first and second inlet passages respectively communicating with said gas and liquid phases and through which metered quantities of said phases are flowable for admixing in said chamber, said assembly including valve means for controlling release of mixed liquid and vapor from said chamber to form a non-flammable spray.

2. The invention as defined in claim 1 in which said organic solute is a resin.

3. A package comprising a pressure container, a pressurized gas phase in the upper interior of the container, a liquid composition in the container below said gas phase, said liquid composition consisting essentially of between about 30 and 80 percent of a liquid aqueous phase and the balance a liquid non-aqueous phase, said phases in static condition being essentially separate from each other, said aqueous phase being adapted to dissolve an organic solute and comprising between about 30 and 90 percent water and between about 70 and 10 percent alcohol of the group consisting of ethyl alcohol and isopropyl alcohol, said non-aqueous phase comprising between about 30 and 70 percent low-hydrolyzing liquified normally gaseous halogen-substituted propellant and between about 30 and 70 percent liquid hydrocarbon of the group consisting of propane, isobutane, normal butane, 2,2, dimethyl propane and isopentane, said gas phase comprising both halogen-substituted and hydrocarbon components, and a dispensing assembly carried by the container and including a mixing chamber having first and second inlet passages respectively communicat-

ing with said gas and liquid aqueous phases and through which metered quantities of said phases are flowable for admixing in said chamber, said assembly including valve means for controlling release of mixed liquid and vapor from said chamber to form a non-flammable spray.

4. The invention as defined in claim 3, in which the ratio of the vapor pressure of said halogen-substituted propellant to the vapor pressure of the hydrocarbon is between about 4 to 1 and 1 to 1.

5. The invention as defined in claim 3, in which said aqueous phase contains between about 1.0 and 8.0 percent (of the aqueous phase weight) of dissolved water soluble resin.

6. The invention as defined in claim 3, in which said assembly includes also a secondary mixing chamber, a third passage controllable by the valve means to pass fluid from the first-mentioned mixing chamber into the secondary chamber, and a fourth spray passage to which the fluid is delivered from said secondary mixing chamber, said first, second, third and fourth passages being formed respectively by first, second, third and fourth orifices, said first orifice diameter being between about 0.0075 inch and 0.0260 inch and the orifice diameter ratios (assigning unity to the first orifice diameter) are substantially:

$$\frac{\text{First orifice}}{\text{Second orifice}} = 0.9 \text{ to } 3.0$$

$$\frac{\text{First orifice}}{\text{Third orifice}} = 1.2 \text{ to } 6.0$$

$$\frac{\text{First orifice}}{\text{Fourth orifice}} = 1.0 \text{ to } 3.0$$

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,995,278

August 8, 1961

Clarence Clapp

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 7, line 23, after "liquid" insert -- aqueous --.

Signed and sealed this 26th day of December 1961.

(SEAL)

Attest:

ERNEST W. SWIDER

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