United States Patent Office 2,871,526 Patented Feb. 3, 1959

2,871,526

POROUS CONTAINERS FOR THICKENED AIR ODOR CONTROL LIQUIDS

Jack J. Bulloff, Dayton, Ohio, assignor to Interstate Sanitation Company, Inc., Cincinnati, Ohio, a corporation of Ohio

No Drawing. Application October 4, 1955
Serial No. 538,520

1 Claim. (Cl. 21—108)

This invention relates to the use of porous containers in dispensing vapors for air odor control.

Holders have been used for solid air odor control agents such as paradichlorobenzene or the solidified liquids described in my application Serial No. 526,771, filed Aug. 5, 1955. Wick dispensers, or refilling well dispensers have been used for liquid air odor control agents such as aqueous formaldehyde solutions, volatile organic agents, or the stabilized liquids described in my application Serial No. 526,772, filed Aug. 5, 1955. Each class of device is suited only to the kind of agent for which it is designed.

This invention relates to devices which are not restricted to one state but which may be used with solids or liquids, or with intermediate consistency states such as rheoplastic jellies or thickened fluids or other semi-solid or semi-liquid air odor control agents. Essentially, it relates to devices employing a porous material for part or all of the container holding the air-odor control material to be dispensed.

In the usual dispensers for solids or liquids, not only is the use of materials of intermediate consistency such as soft waxes, creams, pastes, viscous fluids or two-phase mixtures difficult or impossible, but the vaporization rate is governed by a set of factors which cannot be fixed with sufficient constancy so that the active life of the fill can be predicted with sufficiently reasonable accuracy to warrant a commercial guarantee. For a given air odor control material, with a fixed vapor pressure curve and a set evaporating surface area, the following use variables occur which are difficult to control when conventional dispensers are used:

First, evaporation increases resulting from air movements are erratic in nature. Winds, draughts, fans and moving people set up eddies which disturb the evaporation characteristics of the exposed material. Metal shields with holes currently used to protect air odor control materials from air currents and vision do ameliorate such effects somewhat, but convection currents still reach the relatively exposed evaporating surface of the air odor control material.

Second, evaporation changes resulting from ambient temperatures in the air odor control material dispenser, and in the moving air sweeping it, are also very marked. Because of the complex interactions attending, again no prediction of use rate evaporation can be made from laboratory control evaporation tests on a given air odor control material.

My invention relates to the use of porous containers whose contents are not disturbed unduly in their evaporation rate by the effects of air currents and ambient temperature changes therein. In such porous containers, the efflux of evaporating material is diffusive rather than convective, and incidental moving air sweeping over the container does not enter therein except by diffusion in the same manner as still air.

Rigid materials such as metal, wood or plastic composition, with holes made by tools such as drills, punches or presses, or formed or cast with macroscopic holes permit convective evaporation at rates far exceeding diffusive evaporation, and are not the subject of this invention. Nor are flexible containers of coarse structure such as jute or burlap sacking, perforated polyethylene sheet, or coarsely woven cloths or textiles the subject of this invention for they permit an excess of convective transfer between air external to their enclosure and vapors contained within. This invention is concerned with containers using materials of such fine porosity that convective vapor transfer is so small as to be essentially non-existent whilst diffusive vapor transfer falls within the limits desired.

This invention is further concerned with providing containers that in some measure aid in governing the rate at which air odor control materials enter into the air space to be deodored or reodored. At the same time, the porosity of the materials out of which such containers are made must either be such that the air odor control composition placed therein is not at the same time capable of draining therethrough by hydrostatic pressure, or else the container must be only partly porous so that too-fluid contents therein rest on or impinge against essentially non-porous components.

While a given material may be made up in several porosities, I have found it better to consider a number of materials, each of which has a range of porosities. In this way, for each type or kind of air odor control filling used, an optimum choice can be made for not only porosity, but also for weight, size, shape and appearance of the dispensing container, and for chemical resistance requirements imposed by the nature of the filling itself.

The materials so considered are many and a partial list of them includes the following:

1. Micropore materials
   - Sintered powdered stainless steel
   - Sintered powdered "Kel-F" (a commercially available polyhalogenated ethylene)
   - Sintered powdered "Teflon" (polyfluorinated ethylene marketed by DuPont)
   - "Porex" (a transverse compacted metal wire marketed by General Motors Co.)
   - "Poroloy" (collinearly crossed compacted metal filaments marketed by Poroloy, Inc.)
   - Sintered metal fibers (Armour Inst.)
   - "Porostone" (aloxites of the Carborundum Co. compacted and marketed by the Adams Co.)
   - "Alundum" (a refractory aluminum oxide marketed by Norton Co.)
   - "Aloxite" (aluminum oxide; marketed by The Carborundum Co.)
   - Open "Foamglas" (foamed glass having connecting holes or pores permitting vapor passage and marketed by Owens-Illinois Corning Glass Co.)
2. Plastic foams
   - (*a*) Polyurethanes
     - "Urafoam" (Atlas Powder Co.)
     - "Cush-N-Foam" (foamed polyurethane; the Hudson Co.)
     - Fashion Foam IS (General Tire)
     - Armofoam (Armour)
     - Polyester foams (marketed by various companies)
   - (*b*) Extracted Vinyl Plastisols
     - Elastofoam
3. Woven cloths
   - (*a*) Metallic
     - Stainless Steel
     - Nickel
     - Copper
     - Glass, metallized

Natural fiber, metallized
Cotton
Synthetic bar, metallized
Nylon
"Orlon" (acrylonitrile polymer; DuPont)
"Dynel" (copolymer of acrylonitrile and vinyl acetate; Union Carbide & Carbon Co.)
"Saran" (copolymer of polyvinyl chloride and polyvnylidene chloride; Dow Chemical Co.)

(*b*) Non-Metallic
Glass fiber
Natural fiber
Cotton
Synthetic fiber
Nylon
"Orlon"
"Dynel"
"Saran"
"Kel-F" (poly - monochlorofluorethylene; M. W. Kellogg Co.)
"Teflon" (poly - tetrafluorethylene; Du Pont)

Rigid materials in the above list may be used as such in fabricating bottles, cylinders or other containers whilst flexible materials may be used similarly if reinforced internally or externally by wire, mesh or other material conferring rigidity or strength to the whole. Or, if required, the materials may be used for only part of the container, e. g. top, top and upper walls only, or in some part or parts of a specified container as required for the contents selected or the use desired.

This invention relates not only to the provision of containers for steady even-rate evaporation from dispensers situated in locations where air movement is incidental but also in locations where the evaporating device is deliberately situated in the path of an air stream such as that of a fan, a ventilator, an air conditioner, or the like, so that the stream of air passing the container will carry the vapors of the active odor controlling agent with it to assist in deodorizing or reodoring air throughout a large area or volume as in a theater, assembly hall, railroad car, ship's hold, airplane seating cabin, factory floor, processing bay, restaurant, department store, warehouse, or the like. In this latter use, the selected porosity of the container material used can be further of value in controlling the rate of odoring or deodoring beyond that obtainable by shaping the air odor control filling geometrically or by changing its evaporation rate by compounding.

The pressure differential acting to produce flow of vapor through a porous material, if the vaporizing material is encased, is proportional to the vapor pressure of said vaporizing material. Thus, if a material is quite volatile, its rate of flow through a given porous barrier would be high, and the filling would soon be exhausted by evaporation. On the other hand, if a barrier of smaller porosity is taken, a slower, more amenable rate of filling exhaustion can be imposed in a given situation. Thus, another object of this invention is to provide containers for air odor control and air sanitizing agents ordinarily considered far too volatile for prolonged periods of usage in a forced draft system, such as aqueous formaldehyde solutions.

A still further object of this invention is to provide containers from which neither spray nor dust is dispersed by violent passages of air.

For a vapor pressure diffusion force equivalent to 0.06" Hg, micro-metallic stainless steel of 35 micron average pore diameter permits 10 times as much vapor to pass as for 5 micron average pore diameter sheeting of the same thickness. Thus the rate of passage of air odor control vapors into moving air can be controlled as desired.

This invention provides not only for dispensers for liquid, semi-fluid, ultra-viscous, semi-solid and solid air odor control agents that may be deodorants and/or odorants and/or reodorants, but also has within its purview the providing of a new dispensing means for such materials containing volatile bactericides, fungicides, insecticides or the like. It is a further object of this invention to provide containers simpler in installation and use and superior in operating practice to presently available containers or dispensers such as hand or mechanical sprays, inverted well evaporations cups, wick dispensers, and other types of dispensers known in the art.

The dispensers made of such materials may be of various shapes and sizes as befits the nature of their employment. The materials for them listed above are always available as flat stock, and a test apparatus for them is readily made by glueing them to a section of Pyrex tubing of about 20 mm. inner diameter. Porosities not given by manufacturers can then be readily measured by measuring with compressed air for fine pore materials and with water for coarser materials. Materials that can stand a loading of 3 p. s. i. or more can be used for most liquids. Materials that are much more porous can not be used without first thickening the liquid to prevent its drainage through the walls of the vessel; this is a better use of such materials than using a complex container porous only above the liquid level, as over-filling or transportation of these latter can be troublesome.

The invention is particularly concerned with methods for controlling air odors by dissemination of the vapors of menthadienes and with combinations of compositions comprising the menthadienes and dispensers therefor for use in said methods.

Ortho-, para- and meta-menthadienes may be present in the compositions. However, para-menthadienes will usually be the active air odor control agent of the composition since it occurs in substantial amount in various crude or commercial extracts which are selected for use in making up the compositions to be dispensed as described because of ready availability and low cost.

The air odor control liquid may be thickened or solidified for use in this method. It may be a commercial terpene containing 40%–95% of the menthadiene having the desired chemical lability. One such liquid is the citrus oil product marketed as "Menthadiene" by the Florida Molasses Co. and which contains about 95% of d-limonene. Other suitable commercial products are coniferous wood extracts containing about 50% of *d, l*-limonene (dipentene). In general, crude or commercial products containing 40% to 95% of the menthadiene, such as the optical isomers *d*- or *l*-limonen, or dipentene, may be used.

The air odor control liquids are preferably stabilized against gumming and odor staling on evaporation prior to any thickening thereof by the inclusion of anti-oxidants which may be present in an amount of 0.0002 to 5% by weight, preferably 0.001% to 2.0% or 3.0%. Suitable anti-oxidants include, for example—

Tenox BHA (butyl hydroxyanisole; marketed by Tennessee Eastman Co.)

National Aniline B (marketed by National Aniline Div. of Allied Chemical & Dye Corp. for use as anti-skinning agent in paints)

NDGC—Essentially nor-dihydroguairetic acid; marketed by Nordigard Corp.

Compound 19—Essentially 2,2'-methylene - di - p-cresol; marketed by Sindar Corp.

Sustane #1, Sustane #1F, Sustane #3, Sustane #3F, Sustane #6 — Mixtures of tertiary butyl hydroxyanisoles with synergists in neutral solvents; marketed by Universal Oil Products Co.

dbpc—Food grade ditertiary butyl-p-cresol; marketed by Koppers Company

Propyl gallate
Ethyl gallate
"Voidox"—Modified food grade tertiary butylated phenol; marketed by Guardian Chemical Corp.

The crude or commercial products containing the menthadienes may be diluted with 5% to 20% or even equal parts of an inert hydrocarbon solvent having a vapor pressure similar to the partial vapor pressure of the menthadienes in the composition. Hydrocarbons that may be used include:

Soltrol 130 (a completely odorless petroleum fraction marketed by Phillips Petroleum Co.)
Shell Sol 72 (a petroleum fraction marketed by Shell Development Co.)
Penn Drake 2251 (a petroleum fraction marketed by Pennsylvania Refining Co.)
Odorless 360 solvent, Odorless Mineral spirits } Standard petroleum fractions
Shell 140 Flash solvent, Shell 140 Solvent, Shell 36 Solvent } Petroleum fractions marketed by Shell Development Co.
Stoddard Solvent
Shell Mineral Spirits (marketed by Shell Development Co.)

The crude or commercial product, such as the coniferous wood extracts, may be fortified with 5–20% or up to equal parts, of a pure menthadiene, such as *d*, or *l*-limonene or dipentene, or with 5–20% or up to equal parts, of a commercial product having a high concentration (90–95%) of a menthadiene of the desired chemical lability. For example, a commercial product containing 50% dipentene may be mixed with "Menthadiene" containing 95% *d*-limonene.

These two-component systems may be further modified by inclusion of the inert hydrocarbon solvent in amounts of 5–20%. Three-component systems in which the crude dipentene or other menthadiene, pure menthadiene or extract containing 90–95% thereof and hydrocarbon solvent are used in equal parts or in any suitable proportions and containing, also, the small amount of stabilizing anti-oxidant may be prepared and dispensed in accordance with the invention.

The air odor control liquids may have mixed therewith deodorants, reodorants, perfumes and/or odor masking materials in amounts of, usually, 2–10% by weight.

The air odor control liquids may be thickened or gelled by means of various materials soluble or dispersible therein with heating or in the cold.

On heating, dipentenes and "Menthadiene" dissolve waxes, and such may be used as a thickening agent for the normally liquid air odor control agent in a concentration and of a melting point to provide a composition of predetermined increased viscosity.

The compositions to be dispensed may comprise natural or synthetic wax. Thus, the following waxes may be used to thicken the air odor control liquid: Borneo waxes (such as Pyrowax, a generic term for an extremely large crystalliod refined petroleum wax obtained from petroleum found in Borneo), palm waxes (such as Ross No. 1 and No. G93, marketed by Frank B. Ross Co.), "Petrolies" (e. g. Crown 700, a high melting microcrystalline wax marketed by Petrolite Corporation), microcrystalline waxes of the type of Bareco Be Square Amber 190/95 (a wax of M. P. 190–195° F. marketed by Bareco Oil Co.), ozokerites like Three Star White (a commercially available top grade bleached mineral ozokerite wax), ceresines (e. g. Salomon's White D–13, one commercially available imitation ceresine wax), and the like.

The finely divided halogenated castor oil product sold by Baker Chemical Company under the trade name "Thixcin" gels dipentenes in the cold to yield a product useful in the instant method of controlling air odors. Waxes of larger particle size, e. g. "Castor Wax" (hydrogenated castor oil, marketed by Baker Castor Oil Co.), "Cenwax Wax A" (hydrogenated castor oil fatty acid, marketed by W. D. Hardesty Co.), "Opalwax 10" (hydrogenated castor oil marketed by DuPont), must be melted into the dipentenes but the products obtained are essentially the same as those obtained using "Thixcin" in the cold.

The Gersthofen waxes (formerly known as the I. G. waxes) are suitable for thickening the air odor control liquids comprising the menthadiene, notably Gersthofen Waxes "O," "E," "OP," "OM," "L," and "S." Relatively small amounts (5–15%) of 35% Gersthofen Wax "S" or of "Thixcin" in a commercial dipentene yields an excellent product.

By melting resinous, plastic or polymeric products into a commercial dipentene or "Menthadiene" or compositions comprising those terpenes, the desired degree of thickening or gelling can be obtained, depending on the amount of solute used per unit volume of solvent.

The thickening or gelling solutes for the air odor control fluids contemplated include polyethylenes, polyethylene lubricants and emulsifiable polyethyelenes of 1.0–40% concentration (depending on the Dow Melt Index No.) and also acrylic resins such as "Lucite," "Acryloids" B–82 and B–72 (polyacrylates of intermediate molecular weight marketed by Rohm-Haas Co.), "Cyclovar" resins (commercially available paracoumaronindene resins) polyvinyl alcohols, polyvinyl acetates like "Elvacets" (such as 40–15 marketed by Du Pont), "Orizon" (a polyethylene molding powder marketed by Monsanto Chemical Co.), rosins both modified and unmodified and including Staybelites (modified wood rosins marketed by Hercules Powder Co.), resins of the types of Monsanto C–3, Dow PS3, "Lustrex" 3 and 15 (marketed by Monsanto Chemical Co.), "Plaskons" (marketed by Semet-Solvay Div. of Allied Chemical Corporation), Piccoumarons and Piccolastics (coal tar resins marketed by Pennsylvania Industrial Chemical and Dye Corporation), "Exons" (marketed by Firestone Rubber Co.), and "Opalon" (marketed by Monsanto Chemical Co.

The air odor control liquids may be thickened or gelled by mixing therewith ethyl celluloses having the ethoxy contents of types G, K, N and T, and the viscosity ranges (standard C. P. S.) of 5, 7, 10, 14, 15, 40, 50, 100, 200 and 500, as obtainable from Hercules Powder Co. and the high melt index ethocels R2 and LTSE marketed by Dow Chemical Co.

All polystyrenes including refractory types like "Styron" 666, 700 and 0 767.6 (polystyrene molding powders marketed by Dow Chemical Co.) are acceptable thickeners for the air odor control liquids.

The polyethylenes Q 940, Q 940.2, Q 941.3, Q 941.7, AC, G, GA, 7, 615, 617A, 629, 630, 631; "Plaskon" 8407, 8406, 8416, 8417 and 8429, "Styrofoam" 22, 23 and Q 907.1 (foamed polystyrenes marketed by Dow Chemical Co.) made up in 5 and 10% solutions in air odor control liquids such as "Menthadiene" or Newport Dicom No. 1 (a commercial dipentene marketed by Newport Co.) at 180° F. are useful products for my present purposes. Solutions of 15–20% concentration have greater viscosity. Gels are obtained at solute concentrations of 25–35%.

Metallic soap gels offer the advantage of being easily made and do not change much in viscosity with temperature change. Aluminum soap gels do not melt in the ordinary sense, and are immune to ambient temperature changes throughout the year.

The best metallic soap gellants for the air odor control liquids or compositions comprising them are aluminum bisoaps or disoaps, and of these the preferred soap is aluminum monohydroxy bis *d*, 1-2-ethylhexanoate sold by various suppliers as "aluminum octoate." The cheaper aluminum naphthenates can be substituted for the aluminum octoate.

The commercial dipentene marketed by Hercules Powder Co. under the designation Hercules dipentene 122 is gelled in five minutes at 50° C. after the addition thereto

of 2% Witco aluminum octoate (marketed by Witco Chemical Co.). With 3–30% of aluminum octoate, the product "Menthadiene" (90–95% *d*-limonen) yields stiffer gels than does the commercial dipentene, but both products are within the scope of this invention and useful in controlling air odors by dissemination of the vapors through dispensers as described herein.

In general, concentrated octoate-menthadiene gels are most conveniently prepared by mixing the menthadiene or composition comprising it with the aluminum octoate in the cold, heating the mixture to 60° C. to set it, and ageing it for 24 hours.

It is possible to thicken the air odor control fluids for dispensation of the vapors from porous containers of the type contemplated by mixing the fluid with one or more of the following or each of the following and a filling agent such as "Solka-Floc" (commercially available finely divided wood cellulose), sawdust, etc. or one or more of the following any of which may be a composite mixture of one or more of its type or class: organoclays, silica, wax, plastics, aluminum soap. In this way, the viscosity, vapor retention, rate of evaporation and crumbling of evaporation residue may be controlled.

As an example, 10 gms. of Bentone 34, 100 gms. Solka-Floc BW 200, 10 gms. aluminum octoate Parsons, 10 gms. Thixcin, 10 gms. Gersthofen Wax S, and 500 gms. dipentene (containing 0.3 g. Tenox BHA as anti-oxidant, 1 ml. of neoneuthocene reodorant and 1 ml. of Nilskin anti-skinning agent) were homogenized and allowed to set for 24 hours. The mass was then heated to 180° F. and, with stirring, 100 gms. of Dow Polyethylene Q 941.4 was dissolved therein. On cooling, a material resulted which had a vapor pressure 90% as high as pure dipentene solvent.

Mixing of attapulgite clays such as "Permagel" and bentonite clays such as "Volclay" (a quick gelling bentonite marketed by American Colloid Co.) and wetting agents like Alrose Amine "O" or "S" (marketed by Alrose Chemical Co.) with the menthadienes or compositions comprising them yields greases which are acceptable air odor control compositions for use in the present method. Organically modified bentonite, e. g. Dutch Boy Bentone 34 (dimethyldioctadecyl ammonium montmorillonite) also produces useful greases when mixed with the air odor control liquids.

For example, a useable grease-like product is obtained when Hercules dipentene 122 is placed in a Waring Blendor, the motor is started, and 14 gms. of Bentone 34 are aliquotted in until the mass has the desired consistency.

Finely divided silica hydrogels or aerosols, such as "Santocel" 54 (Monsanto Chemical Co.), Dow Corning Silica (or the pellets), "Syloid" 244 grade 968 (Davison Chemical Co.) and "Cab-O-Sil" (Godfrey L. Cabot Inc.) may be mixed with the air odor control liquids to obtain weak but non-flowing gels which may be dispensed from containers which retain the gels but permit free passage of the vapors of the liquid into the air.

For example, when about 4.92 gms. of "Cab-O-Sil"

are mixed with 95.08 gms. of "Nelio" dipentene 1-A (marketed by Glidden Paint Co. and containing an anti-oxidant) and the mixture is allowed to stand overnight, a firm, transparent gel of excellent odor stability is obtained. A structurally stronger gel is obtained if 7.8 gms. of the "Cab-O-Sil" are mixed with Dixie steam-distilled dipentenes.

These compositions comprising the air odor control liquids and a sufficient amount of the thickening or gelling agent soluble or dispersible therein to impart the desired gel or semi-fluid character to the composition are used in the present method by placing them in a dispensing device as described and from at least some portion of the exposed surfaces of which the vapors of the air odor control liquid freely diffuse into the surrounding air at uniform, constant rate. The air odor is thus controlled by diffusion of the vapors through the dispenser at a steady uniform rate so that constant control of the air odor is obtained for a maximum period of time from a given mass of the composition.

Compositions used in the method may contain varying amounts of the thickening or gelling agent, such as amounts between 5% and 30% or higher and even up to 50%. The dispensing devices used in this method and having the required porosity and other characteristics may be made of any of the materials specified herein, or any equivalent material, and may have any desired size, shape, wall thickness, and porosity to be selected depending on the consistency of the air odor control composition.

What is claimed is:

The combination consisting of an air odor control composition comprising optically active limonene as an active vaporizable constituent and having a consistency which varies from liquid to solid, and a dispenser for the composition, said dispenser being adapted to hold the air odor control composition in a condition of direct exposure to the air the odor of which is to be controlled, and being formed at least in part of a porous solid material of preselected wall porosity of approximately 35 micron average pore diameter and such that it permits diffusive transfer of the vapors of the active constituent of the air odor control composition directly therethrough to the air the odor of which is to be controlled at a steady uniform rate and without any substantial convective vapor transfer, when the dispenser containing the composition is exposed to conditions which would normally tend to induce convective transfer of the vapors of the active constituent.

References Cited in the file of this patent

UNITED STATES PATENTS

1,027,856	Kocher	May 28, 1912

FOREIGN PATENTS

125,308	Germany	July 20, 1900
496,288	Great Britain	Nov. 21, 1938