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DEODORANT COMPOSITIONS AND THE METHODS OF USE

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This invention relates to air deodorization. It comprises new compositions of matter especially adapted for deodorizing air and a process for deodorizing air.

There are many objectionable odors which are desirably controlled in an ordinary home, the most common of these being cooking, smoking and bathroom odors. Two common approaches to controlling odors have been oxidation of the odoriferous material by means of such oxidizing agents as sulfur dioxide, free chlorine, ozone, and hydrogen peroxide and masking by means of perfumes and other pleasantly odoriferous compounds. The oxidation method is complicated by the corrosiveness of the oxidizing agents which makes it difficult to store and use them. In sufficiently large concentrations in air, these agents can corrode metal and are annoying and even harmful to people. The masking method simply pollutes the air to a greater extent, and a substantial portion of the public finds perfumes themselves objectionable in the concentrations needed to mask objectionable odors. The ideal material for treating odor-containing air is one that leaves little residue and is non-corrosive, odorless, non-staining, non-toxic, non-irritating, and effective.

Accordingly, it is an object of this invention to provide a pressurized deodorant composition for treating air containing objectionable odors.

It is another object of this invention to provide a process for treating air containing objectionable odors.

It is a further object of this invention to provide a preferred pressurized deodorant composition, for treating air containing objectionable odors, which will leave the treated air substantially odorless.

It is a still further object of this invention to provide a pressurized deodorant composition for treating air containing objectionable odors, which is non-toxic and non-corrosive and which leaves little residue.

The pressurized deodorant compositions of this invention comprise from about 0.3% by weight to about 15% by weight of the composition of a deodorant material selected from the group consisting of aliphatic unsaturated hydrocarbons containing from one to three multi-bond carbon to carbon linkages, aliphatic saturated hydrocarbons, and mixtures thereof, said saturated and unsaturated hydrocarbons containing from 12 to 18 carbon atoms, the balance of the composition being an aerosol propellant capable of providing a pressure from about 30 pounds per square inch absolute to about 115 pounds per square inch absolute in the aerosol container, under conditions of normal use. Preferably the propellant is either a mixture of trichlorofluoromethane and dichlorodifluoromethane or isobutane, but other known propellants can also be used as hereinafter more fully described. This deodorant composition is packed in an aerosol container of the conventional types and is used to provide a dispersion of the hydrocarbons in air in an amount not less than about 0.1 part per million and in a concentration sufficient to control whatever odor is in the air.

The deodorant hydrocarbons of this invention are either straight or branched chain, preferably the former. Examples of suitable compounds are: dodecene; tetradecene; hexadecene; octadecene; dodecane; tetradecane; hexadecane; octadecane; octene-1 dimer; propylene tetramer; 3,6-dimethyldecane; 2,4,5,7-tetramethyloctane; octadecyne; and 1,3-tetradecadiene.

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Lower homologs (C_{11} and lower) of these deodorant hydrocarbons are also effective at controlling odors, but they have odors of their own. The higher homologs (C_{19} and above) are much less effective than the C_{12}–C_{18} deodorant hydrocarbons of this invention. In the saturated hydrocarbon series, for instance, the compounds are relatively odorless from octadecane down to and including dodecane. Decane has a positive odor of its own and octane and hexane are objectionable in this regard. On the other hand, homologs higher than octadecane (melting point −30° C.) tend to solidify, particularly under the evaporative cooling effect of an aerosol propellant, and this solidification minimizes their effectiveness in controlling odors, and may clog the valve or orifice of the aerosol container.

Branched chain structures, such as octene-1 dimer and propylene tetramer are also effective at controlling odors. Excessively branched structures, however, tend to have an odor of their own. In addition to the longest carbon chain, there should not be more than about four branch chains having from about one to about two carbon atoms.

Structures containing aromatic or ring configurations have very strong natural odors, and are therefore unacceptable. Olfactory desensitization may also be induced by aromatics, e.g., it is believed that the aromatics in gasoline are responsible for its desensitization power.

The double and triple bonds in the hydrocarbons of this invention can be in the alpha position, conjugated, or otherwise, since it appears that the effectiveness of these compounds depends upon number of carbon atoms in the chain and not upon reactivity or location of the double or triple bond. It will be realized that a selection of the specific deodorant hydrocarbon for the compositions of this invention can be made on the basis of considerations other than those relating to deodorization, such as, cost, availability, odor, and amount of residue.

The deodorant hydrocarbons of this invention are very effective against a wide variety of odors. Some of the more common odors which can be controlled by these compounds are bathroom odors, frying odors, cabbage odors, fish odors, onion odors, ethyl mercaptan, and cigarette odors. The treated air is substantially odorless if the propellant selected is odorless and if no perfume is added to the product.

The compositions of this invention have a very low level of toxicity, and are not irritating to the eyes, nose, or throat. They do not leave a noticeable residue or stain furniture, clothes, etc., under ordinary usage.

The term "deodorization" is a broad one comprising several mechanisms for controlling odors. It is not limited to destruction of the odoriferous materials by chemical reaction, but includes control by adsorption or absorption of the odoriferous material, desensitization of the olfactory nerve, and odor cancellation. The latter mechanism is the phenomenon which occurs when the effects of two separate compounds, at least one of which is odoriferous, cancel out, resulting in an apparent destruction of the odor.

Although it is not desired to be bound by theory, the mechanism of deodorization for the hydrocarbons of this invention is presumed to be odor cancellation. A vapor phase chromatography study of air treated by the compositions of this invention failed to detect any reaction products, which seems to eliminate chemical interaction as the mechanism for odor control. Also, treatment of the human nose with the deodorant hydrocarbon dispersion prior to an exposure to objectionable odors failed to control the odors, which seems to eliminate the possibility that the mechanism for odor control is desensitization of the olfactory nerve. Positive evidence for the proposed theory of odor cancellation includes the results of a test in which an objectionable odor was introduced into one nostril of a subject at the same time that a dispersion in air of the deodorant hydrocarbons of this invention was introduced into the other nostril of the same subject. The odor was controlled (cancelled) as far as the subject was concerned although the odorous air and the air containing the hydrocarbons never came in contact.

The deodorant hydrocarbons of this invention solve many problems. Since they are extremely non-reactive and substantially odorless, it is possible to formulate a wide variety of aerosol compositions. Corrosion has always been a problem in aerosol cans, particularly those made of metal, as for instance, iron, aluminum and the like. The deodorant hydrocarbons of this invention are not corrosive to metals, and therefore, permit a wider selection of materials for an aerosol container than would be possible with conventional oxidizing deodorizing agents. Even the more non-reactive conventional deodorizing agents, such as strong perfumes, often require some kind of anti-oxidant to prevent corrosion and degradation of the deodorizing agent. This is not necessary with the compositions of this invention.

By virtue of the fact that the deodorant hydrocarbons of this invention are not reactive, a wider range of perfumes, sanitizers, and other minor additives, can be included in the formulation than can be included with the conventional deodorizing agents. With conventional deodorizing agents, and especially oxidizing agents, many perfumes are ruined upon prolonged storage.

The odorless nature of the deodorant hydrocarbons of this invention also contributes to their utility (although cancellation of an objectionable odor with the substitution of a less objectionable odor may be desirable in some situations). This permits the formulation of an odorless product or the use of a perfume in a deodorant product without having to consider the effect of the odor of the deodorizing agent. Therefore, the deodorant hydrocarbons of this invention are especially suited for use in an aerosol whereas conventional masking deodorizing agents are not. These deodorant hydrocarbons are unique in combining effective odor control, low odor, and low chemical reactivity.

The concentration range of about 0.3% to about 15% by weight of the product for the hydrocarbons of this invention in an aerosol is set on the basis of performance. With lower concentrations than about 0.3%, the cost to the consumer of using the product would be prohibitively expensive, since to achieve adequate performance, a relatively large amount of the product would have to be used. With larger concentrations than 15%, the residue tends to become objectionable and the odor of some hydrocarbon compounds may become noticeable. Solubility of large concentrations of the hydrocarbons in the propellant may also become a problem with certain propellants such as the chlorofluoromethanes and chlorofluoroethanes. This concentration range is especially important based upon the normal usage of aerosol room deodorants which is about two to three grams per usage.

The aerosol propellant should be selected with care. First it must provide the proper amount of pressure in order to achieve an adequate dispersion of the active "deodorant" material in air. From 0 to 115 pounds per square inch absolute (at about 70° C.) is preferred. Ideally, the propellant is not flammable. From this standpoint, the halogenated hydrocarbons and inorganic propellants are preferred whereas such propellants as N-butane, isobutane, and propane are not. However, some halogenated hydrocarbons such as methylene chloride tend to cause corrosion in metal cans in the presence of water where they react to form hydrochloric acid while N-butane, isobutane, and propane do not. Some halogenated hydrocarbons also have odors of their own which would be unacceptable in an odorless product but which could be tolerated in some perfumed products, and some can also pose a toxicity problem. The inorganic propellants such as nitrogen gas are not suitable from the standpoint that a single phase product is desirable and the deodorant hydrocarbons of this invention cannot form a single phase with the compressed gas inorganic propellants. However, two phase products can be used, although they may require agitation prior to use. From the standpoints of odor, corrosiveness, chemical inertness, flammability, and toxicity, a mixture of trichlorofluoromethane and dichlorodifluoromethane is preferred.

If flammability is not a problem and if lower cost is desirable, the saturated hydrocarbon propellants are useful. Isobutane and N-butane are best from the standpoint of a proper vapor pressure, but propane and pentane are also useful and in mixtures can provide the same vapor pressures as isobutane and N-butane. Mixtures of these hydrocarbon propellants with chloro- and/or fluoro-substituted hydrocarbons can give the proper vapor pressure and eliminate flammability while lowering cost as compared with the pure chloro- and/or fluoro-substituted hydrocarbons.

Other acceptable propellants are vinyl chloride, methylene chloride, trichlorotrifluoroethane, N-hexane, asymmetrical and symmetrical dichlorotetrafluoroethane, chlorotrifluoroethane, trifluoromethane, difluoroethane, chlorodifluoroethane, octafluorocyclobutane, isopentane, N-pentane, N_2O, CO_2, N_2, argon and mixtures thereof. Some of the preceding named propellants do not have a suitable vapor pressure when used alone, but they can be used in mixtures so long as the mixture has a proper vapor pressure and the mixture is compatible.

It will be understood that the propellant must be chosen in view of the finished product, and that such considerations as odor, flammability, toxicity, chemical reactivity, corrosiveness, availability, cost, and vapor pressure of the individual propellant will determine whether it is selected, either alone or as part of a mixture, for a given product.

Once a suitable propellant has been selected, the loading of the aerosol container is carried out by conventional procedures which will not be described here in detail but which may be found in Pressurized Packaging, Herska, A., and Pickthall J., chapter V, pp. 106–123, Academic Press, Inc. (1958).

Suitable additives to the compositions of this invention, but which are not necessary, include perfumes and such anti-bacterial agents as quaternary ammonium compounds (e.g., benzethonium chloride), propylene glycol, triethylene glycol, and halogenated hydrocarbons (e.g., hexachlorophene). A normally solid anti-bacterial agent is preferably used with a non-volatile solvent to prevent the formation of an irritating dust when the composition is sprayed into the atmosphere.

The following examples illustrate the practice of this invention and the advantages which accrue from the compositions and process of this invention.

Example I

The following table compares compositions comprising the various deodorant hydrocarbons of this invention and certain lower homologs based upon the following test method.

Ethyl mercaptan, chopped onions, and cigarette butts were placed, respectively, in three separate one gallon jars. Sufficient odoriferous air from these jars was placed in three similar one gallon jars to create odors of a sufficient strength that it took six 1 to 10 dilutions (one part of the odoriferous air plus nine parts fresh air) to reach a dilution where the odor was not detectable (threshold) in the case of ethyl mercaptan and five such dilutions in the case of the onions and cigarettes. This odoriferous air provided the standard concentrations of odors for this test. 0.5 gm. of pressurized aerosol compositions containing 1% of the test materials listed below and the balance propellant, were sprayed into jars containing these standard concentrations of odors. (The propellant was a 50/50 mixture of trichlorofluoromethane and dichlorodifluoromethane.) The number of 1 to 10 dilutions with fresh air needed to reach a threshold odor for each of the jars was then determined. The same procedure was followed with an aerosol containing only propellant, which served as a blank.

Another set of jars with the same three standard concentrations of odors were injected with 0.5 gm. samples of the aerosol compositions until the threshold odor was reached. This procedure was also followed using the propellant blank.

Thus, in this test there were three numbers obtained for each compound and three numbers for the blanks. The first number was the sum of the number of dilutions required to reduce all three odors (standard concentrations) to a threshold level. The second number was the sum of the number of dilutions required to reduce all three odors to a threshold level after the standard odor concentration had been treated with 0.5 gm. of the test material or blank. The third figure was the sum of the number of 0.5 gm. injections of the test material or blank required to reduce the standard odor concentration to the threshold level.

These three numbers were combined arbitrarily to give a single performance number which reflects the deodorant performance of the individual compound. The sum of the last two numbers of the three is subtracted from the first number to give this performance number. The slight deodorization effect of the propellant is accounted for by computing the performance number for the blank and then subtracting this from the performance number of the test material to give a corrected performance number. This has the effect of making the performance number of the blank equal to zero. All figures in the following table are corrected performance numbers.

	Compound	Number
1	Octene	15
2	Decene	14
3	Dodecene	13
4	Tetradecene	8
5	Hexadecene	9
6	Octadecene	11
7	Decane	10
8	Dodecane	7
9	Tetradecane	8
10	Hexadecane	9
11	Octadecane	11

These examples were part of the screening test and roughly indicate the relative deodorant performance of some of the representative individual compounds of the C_{12}–C_{18} aliphatic hydrocarbons of the compositions of this invention. The good performance numbers of the lower homologs are accounted for in part by the masking effect of their own odor.

Example II

A pressurized aerosol air deodorizing composition was prepared which contained 1.4% 1-hexadecene, 1.0% denatured alcohol, 0.07% hexachlorophene, and the balance a 50/50 mixture of trichlorofluoromethane and dichlorodifluoromethane. The product was packed in a conventional aerosol container. The product itself was substantially odor free.

This product was used on the usual cooking, cigarette and bathroom odors found in the home to provide concentrations of 1-hexadecene ranging from 0.1 to 10 p.p.m. in the air; the product was found to be an effective, odorless deodorant.

Example III

An aerosol air deordorizing composition, packed in a conventional aerosol can, was prepared containing 1.4% 1-hexadecene, 1.0% denatured alcohol, 0.21% of a perfume and the rest a 50/50 mixture of trichlorofluoromethane and dichlorodifluoromethane. The product had only the pleasant odor of the perfume.

This composition was used on the usual home odors and was found to be an effective deodorant.

Example IV

An aerosol air deodorizing composition was prepared with 2.0% 1-hexadecene, 0.0004% pine needle oil, and the rest a 50/50 mixture of trichlorofluoromethane and dichlorodifluoromethane. The composition was packed in a conventional aerosol can. The product itself was substantially odor free to observers.

This composition was used with the usual home odors and found to be an effective deodorant.

Example *V*

An odorless aerosol air deodorizing composition was prepared with 1.5% hexadecane, 0.5% deodorized kerosene, and the rest a 50/50 mixture of trichlorofluoromethane and dichlorodifluoromethane. The composition was packed in a conventional aerosol can.

This composition was used with the usual home odors and was found to be an effective deodorant.

Example VI

An odorless aerosol air deodorizing composition was prepared with 3.0 gm. 1-hexadecene, 1.4 gm. denatured ethyl alcohol, 0.1 gm. hexachlorophene, and 136 gm. of a 50/50 mixture of trichlorofluoromethane and dichlorodifluoromethane and packed in a conventional aerosol container. The product was substantially odor free.

This composition was used on the usual home odors and was found to be an effective deodorant.

Example VII

An odorless aerosol air deodorizing composition was prepared with 4.0% octene-1 dimer and the rest a 50/50 mixture of trichlorofluoromethane and dichlorodifluoromethane. The composition was packed in a conventional aerosol container. The product itself was substantially odor free.

This composition was used with the usual home odors and was found to be an effective deodorant.

All percentages in the preceding examples were by weight of the total product.

Carbon dioxide, nitrous oxide, argon, nitrogen, difluoroethane, isobutane, trichlorofluoromethane, chlorodifluoroethane, octafluorocyclobutane, isopentane, N-pentane, dichlorodifluoromethane, methylene chloride, N-butane, propane, vinyl chloride, and mixtures of the above can be substituted for the propellant in the preceding examples with substantially equivalent results so long as the propellant provides a pressure of from about 30 pounds per square inch to about 115 pounds per square inch absolute under conditions of use except that those propellants with odors provide products with a slight, not unpleasant odor.

Similarly, 3,6-dimethyl decane; 2,4,5,7-tetra methyloctane; octadecyne; 1,3-tetradecadiene; and propylene tetramer can be substituted for the hydrocarbons in the preceding examples with substantially equivalent results.

What is claimed is:

1. A pressurized deodorant composition comprising from about 0.3% to about 15% by weight of the composition of a deodorant hydrocarbon containing from 12 to 18 carbon atoms, said hydrocarbon containing not more than about four branched chains having from about one to about two carbon atoms, and said hydrocarbon being selected from the group consisting of aliphatic unsaturated hydrocarbons containing from one to three multi-bond carbon to carbon linkages, aliphatic saturated hydrocarbons, and mixtures thereof, the balance being an aerosol propellant capable of providing a pressure from

about 30 pounds per square inch absolute to about 115 pounds per square inch absolute in the aerosol container under conditions of normal use.

2. The composition of claim 1 in which the deodorant hydrocarbon is a straight chain compound and the aerosol propellant is selected from the group consisting of isobutane, trichlorofluoromethane, dichlorodifluoromethane, and mixtures thereof.

3. The composition of claim 1 in which the hydrocarbon is hexadecane and the aerosol propellant is a mixture of trichlorofluoromethane and dichlorodifluoromethane.

4. The composition of claim 1 in which the hydrocarbon is octene-1 dimer and the aerosol propellant is a mixture of trichlorofluoromethane and dichlorodifluoromethane.

5. The composition of claim 1 in which the hydrocarbon is 1-hexadecene and the aerosol propellant is a mixture of trichlorofluoromethane and dichlorodifluoromethane.

6. The composition of claim 5 containing a minor amount of pine-needle oil.

7. The process of deodorizing odor-containing air comprising the step of dispersing in air, not less than about 0.1 part per million of said air and in a concentration sufficient to control the odor in said air of deodorant hydrocarbons containing from 12 to 18 carbon atoms, said hydrocarbons containing not more than about four branched chains having from about one to about two carbon atoms, and said hydrocarbons being selected from the group consisting of aliphatic unsaturated hydrocarbons containing from one to three multi-bond carbon to carbon linkages, aliphatic saturated hydrocarbons, and mixtures thereof.

8. The process of claim 7 in which the hydrocarbons are dispersed in air by means of an aerosol propellant.

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