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STABILIZED SOLID GRANULAR PERFUME
COMPOSITION

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9 Claims

ABSTRACT OF THE DISCLOSURE

A method is disclosed for packaging a product scented with perfume in a polyethylene container to prolong the odor life of the perfume which otherwise is completely exhausted in a few days due to its migration through the walls of the polyethylene container. To accomplish this the perfume is adsorbed on metallic particles having a high internal pore volume and a large surface area which are contained in the package.

This invention relates to an improved stabilized perfume and to a package containing a product scented with said perfume. More particularly, the invention relates to a perfume having a long odor life by virtue of its being adsorbed upon a metallic oxide carrier of defined porosity and surface area, and to a polyethylene package containing a product scented with the aforesaid stabilized perfume.

In recent years, the use of polyethylene as a packaging material has met with wide-spread acceptance primarily because of its lightness, lack of taste and odor, flexibility, and its ability to be molded into attractive shapes. However, despite their many assets, polyethylene packages do possess a shortcoming in that polyethylene is not the complete barrier to permeation of vapors as are metal and glass. Thus, it has been found that when perfumed solid materials are contained in a polyethylene package, in a matter of a few months, the perfume is completely exhausted due to its migration through the polyethylene container. Therefore, up to now, it has not been practical to package scented materials, particularly solids, in a polyethylene container for consumer consumption in view of the relatively short shelf life of the product from the standpoint of its odor.

According to the present invention, we have discovered a method of retarding perfume migration through a polyethylene container which makes a polyethylene package substantially equivalent to a metal or glass package in shelf life, without suffering exhaustion of the perfume.

Accordingly, it is an object of the present invention to provide a scented product in a polyethylene container having a long shelf life.

It is another object of the invention to provide a solid granular product in a polyethylene container with said product being in admixture with metallic particles having a high internal pore volume and large surface area, containing an adsorbed perfume.

It is another object of this invention to provide a scented material having a long odor life by virtue of its being adsorbed on a high pore volume and large surface area catalytic carrier.

These and other objects of the invention will become more readily apparent from the following detailed description with particular emphasis being placed upon the example.

In accordance with the present invention, a perfume is adsorbed or absorbed onto and into a metallic material having a high pore volume and large internal surface area. Quite surprisingly, it has been found that a much

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greater quantity of the perfume can be taken up by the material, without losing its free-flowing characteristics, and the perfume released at a much slower rate than when employing the same perfume with the carrier being granular vermiculite, diatomaceous earth, bone ash, silicon dioxide, clay, and the like. The reason for the aforesaid superiority is not completely understood but it is theorized that the perfume is associated with the metallic particles by more than a mere physical attraction. Thus, it is believed that, while there is no primary chemical bonding, some chemical bonding of a secondary nature exists. This theory is at least partially supported in that there is a considerable temperature rise when the perfume and adsorbent material are mixed. The stabilized perfume is added to a solid granular product, such as a toilet bowl cleaner, to impart a pleasant odor, and, the mixture packaged in a polyethylene container. The polyethylene package has a useful odor life substantially equivalent to that of a glass or metal, without having an unduly strong perfume odor at the time of the initial packaging.

The materials employed as the carrier in accordance with the present invention are metal or metal oxide catalytic materials, referred to collectively herein as "metallic" materials, having a distinct pore volume, large internal surface area, and which are inert to the product which is to be admixed with the stabilized perfume. Specific examples of carrier materials are the synthetic or semi-synthetic petroleum cracking catalysts of high surface area and high pore volume. Illustrative materials of the above type include admixtures of alumina and silica, in substantially any ratio. Other catalytic materials can be employed. Specific materials found particularly advantageous are (1) a microspheroidal material comprising about 13% alumina, 86.8% silica with the remaining 0.2% comprising salts and traces of heavy metals as impurities; (2) a silica gel having a pore volume of 1.10 ml./gr. and a surface area of 750-850 square meters per gram; (3) a gelled alumina having a pore volume of .20 ml./gr. and a high surface area; and, (4) synthetic zeolites, often referred to as molecular sieves, described in U.S. Patent Nos. 2,818,137 and 2,818,455, which are highly porous alkali metal alumina silicates having pores of molecular dimensions and uniform size. It is, of course, apparent that other metals or their oxides can be present in the carrier, or used as the carrier. In general, elemental materials, their oxides, and mixtures thereof, are operable. Mixtures of zinc, copper, chromium, nickel, cobalt, iron, ruthenium, and thorium either in the elemental state or as oxides either individually or in combination, can be used. As will be apparent from the discussion hereinafter, the high pore volume and large surface area of the materials, normally obtained by spray drying the catalytic materials, are the controlling characteristics.

The essential features of the catalytic carrier, as noted hereinbefore, are the internal porosity and/or the total pore volume of the material, and the total surface area of the particles. Thus, the metal particles will contain many minute openings or crevices which extend into the particles. The perfume to be adsorbed will collect in these crevices or openings, apparently bonded by more than mere physical attraction. The perfume, being held internally, is only slowly released from the metal particles in substantially controlled amounts. In addition to the slow release, a second noteworthy advantage of the internal adsorption is that most of the perfume, not being held on the surface of the catalytic particles, is insulated or held away from the material being packaged and scented. Preferably, therefore, the pore volume should be at least approximately 0.20 ml./gr. with the upper limit only being dictated by the materials commercially available. Therefore,

as a practical matter, the pore volume will be from 0.20–1.50 ml./gr. of the catalyst when calcinated at 1,000° F. for three hours. The pore volume can be determined by adsorption or absorption of nitrogen on the material at the temperature of liquid nitrogen in a standard B.E.T. apparatus. Additionally, the actual amount of perfume collected on the particles can be determined by weighing the particles and thereafter saturating the particles with perfume and again weighing the particles to note the increase in weight. The surface area of the particles should be in the neighborhood of at least 150 square meters/gram, with the upper limit not being critical. However, from the practical standpoint, the surface area will be from about 150 to 1050 square meters/gram, again when calcinated at 1,000° F. for three hours or substantially equivalent treatment. Although the particle size is not particularly critical, it is preferred that the particles be relatively fine, but still not sufficiently fine to be considered a powder. Additionally, it can be said that pore diameter of the crevices should be as small as possible and still have a large over-all porosity, i.e., it is preferred that there be a large number of small openings to obtain a given porosity, rather than a smaller number of large openings. This, of course, is determined to some extent by the nature of the perfume which is to be adsorbed and the size of its molecule.

The perfumes which can be employed herein are not particularly critical and can be any material which is readily adsorbed by the catalytic particles and which are slowly released. Suitable perfumes include the alcohols, aldehydes, esters, ketones, ethers, phenols, and lactones. Additionally, it is possible to use complex mixtures of the aforesaid classes of perfumes. Perfumes which have been found particularly advantageous for scenting a product such as a toilet bowl cleaner include methyl salicylate, propenyl phenyl methyl ether, phenyl propyl aldehyde, phenyl ethyl alcohol, p-methyl acetophenone, and carvacrol. The materials are readily adsorbed by the catalytic carrier and are only slowly emanated.

The perfume can be added to the catalytic materials in varying amounts to obtain the desired concentration of the perfume, usually from about 12 to 65% of the total weight of the stabilized perfume. However, under normal circumstances, the perfume is added in a volume sufficient to completely or substantially completely fill the pore voids of the catalytic material. Thus, the perfume is added to a point just before the catalytic material starts to cake. The catalyst then retains its original characteristics of free flow and is easily blended with the product to be scented.

The stabilized perfume can be employed with any solid granular material which does not characteristically have a pleasant odor and wherein it is desirable, from the standpoint of consumer appeal, to impart a pleasant scent. Since a substantial percentage of the perfume is internally adsorbed by the catalytic carrier, thus being insulated, or held away from the material being packaged and scented, there is less opportunity for reaction between the perfume and the packaged product. For example, it has been found that toilet bowl cleaners of the sodium bi-sulphate type can be physically admixed with the stabilized perfume and packaged in a polyethylene container with the perfume only slowly emanating, providing a long shelf life. Another area of use is in plastic scouring pads.

Having described the invention in general terms, the following example is set forth to more particularly illustrate the invention.

EXAMPLE

A microspheroidal catalytic material composed of 13% alumina, 86.8% silica, and the remaining 0.2% being salts and heavy mineral impurities, having a pore volume of 0.88 ml./gr. and a surface area of 500 square meters/gram, was admixed with methyl salicylate in a ribbon mixer at a ratio of 1.0 part catalyst to 0.9 part perfume. During the admixture, there was a heat rise of 20 to 25°

F. for a ten thousand-gram, or 22-pound mix. The resultant stabilized perfume was dry and free flowing.

1.2 parts of the stabilized perfume was added to 100 parts of toilet bowl cleaner composed of 75% sodium bisulphate, 11% sodium carbonate, 11% sodium chloride, and 3% inert materials. The total granular composition was poured into a polyethylene container having a wall thickness of .030–.045 inch and the container sealed. The product retained its pleasant scent for more than 30 days in an accelerated test, wherein the package was placed in an air-circulating oven at 125° F.; equivalent to approximately six months of normal shelf life.

An identical product merely scented with an equivalent amount of liquid perfume showed no trace of the perfume odor after only 3 days under the same test conditions.

Employing a similar procedure, the methyl salicylate was admixed and adsorbed onto vermiculate having 98% of the particles between 4 and 30 mesh on the Tyler scale. The product, when admixed with the toilet bowl cleaner composition described above and subjected to identical test conditions in a polyethylene container had a shelf life of only 4 days. When the vermiculite was replaced with diatomaceous earth, bone ash, and silicon dioxide, substantially identical results were obtained.

As is apparent from the above tests, the stabilized perfume prepared in accordance with the present invention had a greatly prolonged odor life. Thus, the entrapment and slow release of the perfume in accordance with the present invention has solved a long-standing problem for those who wish to package a scented solid in polyethylene.

In the above example, the perfume can be replaced by other perfumes including aldehydes, esters, ketones, ethers, and phenols. Additionally, the carrier can be replaced by other metal carriers provided the material possesses a total pore volume and surface area in the range hereinbefore defined. The solid granular material packaged with the stabilized perfume can be any solid material in which it is desirable to impart a pleasant scent.

What is claimed is:

1. A stabilized solid granular perfume composition comprising 12–65 percent by weight of a granular catalytic material taken from the group consisting of zinc, copper, chromium, nickel, cobalt, iron, ruthenium, thorium, the oxides of said metals, alumina and silica, said material having a pore volume of at least 0.20 milliliters per gram and a surface area of at least 150 square meters per gram with a perfume contained on said material.

2. The stabilized perfume composition of claim 1 wherein the pore volume of said granular catalytic material is from 0.20–1.50 milliliters per gram and the surface area is from 150–1050 square meters per gram.

3. The stabilized perfume composition of claim 2 wherein the catalytic material is composed of alumina and silica and has a pore volume of .90 milliliters per gram.

4. The stabilized perfume composition of claim 3 wherein the perfume is selected from the group consisting of methyl salicylate, propenyl phenyl methyl ether, phenyl propyl aldehyde, phenyl ethyl alcohol, p-methyl acetophenone, and carvacrol.

5. The stabilized perfume composition of claim 1 wherein said granular catalytic material consists of a microspheroidal material comprising about 13 percent alumina and about 86.8 percent silica.

6. The stabilized perfume composition of claim 1 wherein said granular catalytic material consists of a silica gel having a pore volume of 1.10 ml./gram and a surface area of 750 to 850 square meters/gram.

7. The stabilized perfume composition of claim 1 wherein said granular catalytic material consist of gelled alumina having a pore volume of .20 ml./gram.

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8. The stabilized perfume composition of claim 1 wherein said granular catalytic material consists of a highly porous alkali metal alumina silicate.

9. A solid granular toilet bowl cleaner comprising 75 percent sodium bisulphate, 11 percent sodium carbonate and 11 percent sodium chloride and a stabilized perfume composition as claimed in claim 1.

References Cited

UNITED STATES PATENTS

2,519,665	8/1950	Klippert	-----	167—94	XR
2,525,497	10/1950	Monfried	-----	206—46	XR
2,564,860	8/1951	Ryberg	-----	167—94	XR

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2,778,774	1/1957	Buslik	-----	167—94
3,214,221	10/1965	Finnegan	-----	206—46 XR
3,215,719	11/1965	Allen et al.	-----	167—94 XR

FOREIGN PATENTS

1,114,613	10/1961	Germany.
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