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METHOD FOR PROLONGING THE ODOR OF PERFUMED MATERIALS WITH TRIMETHYLNORBORNYL-ALKYLCYCLOHEXANONES

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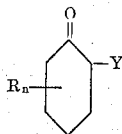
9 Claims. (Cl. 167-94)

This invention relates to a method for sustaining or prolonging the odor of perfumed materials. More particularly, this invention is directed to a method for prolonging the odor of perfumed soap compositions and to perfume-containing soap compositions which have been stabilized against odor loss.

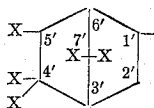
While the incorporation of perfumes into materials to impart a pleasant or odorous nature thereto has its origin in ancient times, this practice has, nevertheless, recently become of considerable importance and today is one of the most rapidly growing industrial procedures for improving commercial products of every description. For example, perfumes are incorporated into such diverse materials as plastics, papers, soaps, diesel fuels, and laundry bleaches, not only for the purpose of rendering such materials pleasantly odorous, but also to mask undesirable and offensive odors inherently possessed by such materials. In this procedure of enhancing commercial products, it is, of course, obvious that the odor induced into the product should be long lasting and not rapidly fade or disappear so as to nullify the costly perfume addition. It is all too frequently the case, however, that perfumed materials, and particularly perfumed soap compositions, rapidly lose their odor. This rapid odor loss may be avoided, however, and the odorous nature of perfume materials greatly prolonged, particularly in the case of perfumed soap compositions, by incorporating into such materials a stabilizing compound according to the method of this invention.

Accordingly, an object of this invention is to provide a method for prolonging the odor of perfumed materials. Another object is to provide a method for prolonging the odor of perfumed soap compositions by incorporating into such compositions a stabilizing compound. A still further object is to provide perfumed soap compositions stabilized against loss of their odorous nature. These and other objects of this invention will be apparent from the further detailed description thereof.

The odor of perfumed materials is prolonged according to this invention by incorporating into such materials a cyclohexanone compound of the following formula:



wherein n is an integer of from 0 to about 2, Y is an alkyl group and R is a member selected from the group consisting of alkyl, cycloalkyl, aryl and a trimethylnorbornyl radical of the formula:



wherein X is selected from the group consisting of hydrogen and methyl radicals, provided at least three X 's are methyl. Examples of the compounds which may be used either individually or in admixture, according to this

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invention, to prolong the odor of perfumed materials, and having the above general formula, include:

- 2-dodecylcyclohexanone,
- 2,6-didodecylcyclohexanone,
- 2,4,6-triethylcyclohexanone,
- 2-cyclopentyl-6-methylcyclohexanone,
- 2-phenyl-6-methylcyclohexanone,
- 2-(6',7',7'-trimethylnorborn-1'-yl)-6-methylcyclohexanone,
- 2-(6',7',7'-trimethylnorborn-1'-yl)-6-ethylcyclohexanone,
- 2-(4',4',5',6'-tetramethylnorborn-1'-yl)-6-ethylcyclohexanone,
- 2-(4',4',5'-trimethylnorborn-1'-yl)-6-methylcyclohexanone,
- 2-(4',4',5'-trimethylnorborn-1'-yl)-6-ethylcyclohexanone,
- 4-(4',4',5'-trimethylnorborn-1'-yl)-6-methylcyclohexanone,
- 4-(4',4',5'-trimethylnorborn-1'-yl)-6-ethylcyclohexanone,
- 4-(6',6',7'-trimethylnorborn-1'-yl)-6-methylcyclohexanone,
- 4-(6',6',7'-trimethylnorborn-1'-yl)-6-ethylcyclohexanone,
- 3-(4',4',5'-trimethylnorborn-1'-yl)-6-methylcyclohexanone,
- 3-(6',6',7'-trimethylnorborn-1'-yl)-6-ethylcyclohexanone, or
- 2,4-di-(4',4',5'-trimethylnorborn-1'-yl)-6-methylcyclohexanone.

The compounds represented by the above general structural formula, which may be incorporated into a perfumed material to prolong its odorous nature, may, in general, be prepared according to conventional procedures. For example, where R of the above formula is an alkyl, a cycloalkyl, or an aryl radical, the compounds having such substituents may be prepared by mono-, di-, or tri-alkylating a 2-lower alkyl substituted cyclohexanone, for example, 2-methylcyclohexanone with the appropriate alkylating agent. When the R substituent is a trimethylnorbornyl radical which represents the preferred substituent of this invention particularly when the Y substituent is a lower alkyl group of from 1 to about 5 carbon atoms, for example methyl or ethyl, the compounds having such substituents may be prepared by first alkylating an ortho-alkylphenol, for example ortho-cresol, with camphene under Friedel-Crafts conditions. The alkylation product thus obtained, comprising a trimethylnorbornyl substituted ortho-alkylphenol, is then hydrogenated to the corresponding tri-methylnorbornyl substituted 2-alkylcyclohexanol which, in turn, is dehydrogenated or oxidized to produce the desired trimethylnorbornyl substituted 2-alkylcyclohexanone which for purposes of convenience is alternatively referred to herein as trimethylnorbornyl substituted 6-alkylcyclohexanone. The trimethylnorbornyl substituted 2-alkylcyclohexanone prepared by this procedure is usually obtained as a mixture of isomers. For example, in the case of monoalkylation, that is where n in the above formula is an integer of 1, the 6-alkylcyclohexanone may be substituted with the trimethylnorbornyl radical in one of the 2, 3 or 4 positions. The trimethylnorbornyl radical itself also exists in isomeric forms and the methyl groups, with the junction carbon atom of the norbornyl radical being designated the 1' position, may be located in the 4',4', and 5' positions or the 6', 7', and 7' positions. The compound may also exist in the exo and endo forms and the different substituents may also exist in cis and trans configurations. All of these isomeric forms may be used as the stabilizing compound either individually or in admixture.

The perfumed materials to which a compound having the above general formula may be added according to the method of this invention to prolong the odor thereof, in general, comprises any substance to which a perfume is added to induce a pleasant odor. As used herein the term perfume means a mixture of synthetic or naturally derived organic compounds including, for example, alcohols, aldehydes, ethers, ketones, esters and frequently also hydrocarbons which are combined in fixed proportions so that the odor of the individual compounds combine to produce a harmonious fragrance. In perfumery practice, these compounds are combined through the blending of natural essential oils, gums, resins, animal derivatives, absolutes, natural isolates and synthetic chemicals. Examples of materials to which perfumes of this description are added to induce a pleasant odor thereto, and to which a stabilizing compound of the above formula may be added to prolong the odorous nature thereof include plastics, paper products, leathers, cosmetic creams, synthetic and natural detergents, talcum powders or soap compositions.

Of the various perfumed materials into which a stabilizing compound may be incorporated according to this invention to prolong the odor thereof, perfumed soap compositions are the materials most dramatically affected by such incorporation and are the most suitable perfumed materials to be treated according to this invention to prolong their odorous nature. The precise reason why incorporation of a stabilizing compound, and particularly a trimethylnorbornyl substituted alkylcyclohexanone, into a perfumed soap composition has the effect of prolonging its odor is not completely understood at this time. It is believed, however, based upon present reasoning, that the stabilizing compound in some way prevents interaction of the perfume and the soap constituents and prevents the normal breakdown of the soap constituents both of which usually shorten the odor life of perfumes in soap.

The soap compositions which may be treated according to the method of this invention are the familiar soaps which are used principally for washing or emulsifying purposes and in general consist essentially of sodium or, more preferably, the potassium salts of fatty acids having from about 12 to 18 carbon atoms per molecule. These soaps may be prepared according to any of the well known preparational procedures which, in general, involve saponifying fats and oils or neutralizing fatty acids with sodium or potassium hydroxide or carbonate to obtain a crude soap which is subjected, particularly in the case of toilet soaps, to milling and plodding, prior to being formed into bars, chips or powders. The perfume used to scent the soap is usually incorporated into the soap during the milling stage of the preparation and generally is added in an amount of from about 0.5 to 5 percent by weight with an amount of about 0.75 to 1.25 percent being more commonly used.

The stabilizing compound may be incorporated into the perfumed material in various ways. For example, in the case of perfumed soap compositions, the stabilizing compound may be incorporated into the soap during the milling stage of the preparation or the stabilizing compound may be premixed with the perfume and incorporated into the soap at the same time as the perfume. The amount of the stabilizing compound added to the perfumed material will vary depending upon the particular material, the amount of perfume contained therein, and the particular stabilizing compound used. In the case of perfumed soap compositions, where a trimethylnorbornyl substituted 2-alkylcyclohexanone is used, the amount added may range from about 0.005 to 0.06 percent based upon the weight of the soap with an amount of from about 0.02 to 0.04 percent being satisfactorily used in most instances.

The particular stabilizing compound utilized and the success thereof in prolonging odor will vary depending, in part, upon the particular perfumed material being treated. In the case of the perfumed soap compositions, the most

dramatic results are obtained when the stabilizing compound is a trimethylnorbornyl substituted lower alkylcyclohexanone, that is, where in the above general formula R is a trimethylnorbornyl radical and Y is a lower alkyl group, for example, methyl or ethyl. This compound is accordingly the preferred stabilizing compound to be used according to the method of this invention, particularly to prolong the odor of perfumed soap compositions.

As hereinbefore indicated, the trimethylnorbornyl substituted alkylcyclohexanone, due to its method of preparation, exists as a mixture of isomers with the principal isomer in the case of monoalkylation most likely being a 6-alkylcyclohexanone substituted in the 2 or 4 position with a 6',7',7'-trimethylnorborn-1'-yl radical admixed with smaller amounts of the 3 position isomer as well as quantities of 6-alkylcyclohexanone substituted in the 2 or 4 position as well as the 3 position with a 4',4',5'-trimethylnorborn-1'-yl radical. Of these various isomers, which also include the exo and endo forms, and cis and trans configurations, it is believed that the 6-lower-alkyl, preferably methyl, cyclohexanone substituted in the 2 position with a 4',4',5'-trimethylnorborn-1'-yl radical is the most active isomer for prolonging odor. However, as previously indicated, it is not usually necessary to utilize costly and tedious separational procedures to isolate any particular isomer as a mixture of isomers may be suitably utilized in most instances as the stabilizing compound.

The following examples are given to illustrate the method of this invention to prolong the odor of perfumed materials and to perfumed materials stabilized against odor loss, but they are not intended to limit the scope of this invention in respect to the illustrated stabilized compounds or to the perfumed materials stabilized:

EXAMPLE I

A stabilizing compound was prepared for use according to the method of this invention to prolong the odor of perfumed material as follows:

About 1300 grams (12 mols) of ortho-cresol, about 560 grams of heptane and about 865 grams of polyphosphoric acid were added with mixing to a reaction flask over a period of about 15 minutes with the temperature maintained by cooling at about 25° to 30° C. Then about 681 grams (5 mols) of camphene mixed with about 190 grams of heptane were added to the flask. After mixing for about 7 hours at a temperature maintained at about 25° to 30° C., the mixing was stopped and the mixture allowed to stand until it separated into organic and inorganic layers. The inorganic layer was extracted with about 500 grams of heptane and the heptane extract combined with the organic layer and the combined organic mixture was then washed with about a liter of water. Sodium carbonate was added to neutralize any remaining acid and the organic mixture thereafter dried by azeotropic distillation. The remaining mixture was then fractionated to recover about 953 grams of trimethylnorbornyl substituted ortho-cresol boiling at 168° C. at about 1 mm. Hg and having a refractive index of n_D^{20} 1.5465. About 871 grams of this product were then changed to an autoclave containing about 87 grams of a nickel catalyst. The product was then hydrogenated at about 160° C. and 600 p.s.i. hydrogen pressure for about four hours. The hydrogenation product was removed and washed with isopropanol. After flashing off the isopropanol, the hydrogenation product was fractionally distilled to recover about 775 grams of trimethylnorbornyl substituted 2-methylcyclohexanol boiling at about 125° C. to 138° C. and having a refractive index of n_D^{20} 1.4975 to 1.5072. About 670 grams of this product were then changed to a reaction flask containing about 1820 grams of water. With mixing, the mixture was heated to about 60° C. and then over a period of about one half hour were added about 570 grams of a 70 weight percent aqueous sodium dichromate solution and about 1050 grams of a 50 percent sulfuric acid solu-

tion. The temperature of the exothermic reaction was maintained at about 60° C. for about one hour and then the mixing was stopped and the mixture allowed to stand. The resulting aqueous layer was separated, extracted with heptane and the heptane extract combined with the organic layer which was thereafter neutralized with carbonate. After removal of the heptane, the remaining mixture was subjected to fractional distillation to recover about 414 grams of trimethylnorbornyl substituted 2-methyl cyclohexanone boiling at about 136° C. at 1 to 2 mm. Hg pressure and having a refractive index of N_d^{20} 1.4980 to 1.5000.

EXAMPLE II

The following test was conducted to demonstrate the odor prolongation of perfumed materials according to this invention:

The following perfumes were prepared:

Perfume A—Rose

Component:	Parts by weight
Citronelloj	45
Citronellyl acetate	6
Benzophenone	5
Nerol	10
Linalool	5
Hydroxy citronellal	10
Phenylethyl alcohol	3
Phenylethyl dimethyl acrylate	3
Oil bois de rose	8
Isoeugenol	1/2
Oil caraway	1/2
Aldehyde C-9, 10% alc.	1/2
Isomenthol	1 1/2

Perfume B—Lavender

Component:	Parts by weight
Camphene 97%	3
Alpha-pinene	1
Linalool oxide	1/2
Etyhl amyl ketone	1
Alcohol C-6	1/2
Amyl alcohol	1/2
Methylheptenone	1/2
Isoborneol	2
Alpha-terpineol	3
Nerol	3
Linalool	40
Eucapliptol	1/2
Isobornyl acetate	2
Coumarin	1/2
Terpinyl acetate	2
Terpinyl isobutyrate	1/2
Dimethylacrylic acid	1/2
Vinyloctahydromethanoindinyl acetate	35
Ocimene	3
Oil lemon California	1/2
Oil clove	1/2

Perfume C—Rose Geranium

Component:	Parts by weight
Isomenthone	6
Citronellyl formate	7
Geranyl formate	3
Citronelloj	40
Geraniol	5
Linalool synthetic	3
Rose crystals	1/2
Benzophenone	3
Guaiacwood acetate	1/2
Isobornyl formate	1
Isoeugenol	1/2

Component:	Parts by weight
Alpha-terpeniol	2
Isomenthol	1
Phenylethyl alcohol	5
Styralyl acetate	1/2
Isoamyl formate	1/2
Phenylethyl dimethyl acrylate	1
Ethyl salicylate	1
Methyl hexyl ketone	1/2
Oil cedarwood	5
Phenylacetaldehyde dimethyl acetal	6
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Perfume D—Eau de Cologne

Component:	Parts by weight
Oil petitgrain	10
Oil bergamot	6
Linalyl acetate	20
Terpinyl acetate	25
Oil mandarin	1
Oil marjoram	1
Cedryl acetate	8
Cinnamyl alcohol	11
Isobornyl formate	5
Citronelloj	5
Coumarin	1/2
Oil lavandin	1/2
Benzoin 50% diethylphthalate	1
Yara Yara	1/2
Heptyl formate	1/2
Oil limes distilled	3 1/2
Phenylpropyl alcohol	1 1/2

Each of the above perfumes, A, B, C, and D, was divided into two parts and to one part was added a two weight percent proportion of a stabilizing compound comprising a trimethylnorbornyl substituent 2-methylcyclohexanone boiling from 119° to 124° C. at 0.5 mm. Hg and having a refractive index of N_d^{20} 1.4983 to 1.5003.

Soap cakes were prepared by first mixing about 50 grams of standard toilet soap pellets and about 0.5 gram of perfume. This mixture was then milled and finally plodded by extrusion until it became a plastic mass. The soap mass was then placed in a die and pressed into a cake. Two groups of soap cakes were prepared for each of the above perfumes. The first group contained the perfume without the stabilizing compound and the second group contained the perfume to which the stabilizing compound had been added.

The odors of the stabilized and unstabilized cakes were identical as prepared. The cakes were then exposed to daylight and air indoors over a period of about one month and were examined twice weekly for odor changes. It was observed that the odors of the unstabilized cakes began to fade rapidly and, in all cases, disappeared completely in from one to two weeks time. The odors of the stabilized soap cakes, however, even at the end of the test, were still very strong and unaltered as compared to their original odors.

EXAMPLE III

The following test was conducted to demonstrate the odor prolongation of perfumed materials according to this invention under severe aging conditions:

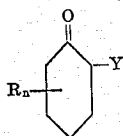
A Rose perfume of the same formula as Perfume A in Example II was prepared and divided into two parts. To one part was added a one weight percent proportion of a stabilizing compound comprising a trimethylnorbornyl substituted 2-methylcyclohexanone boiling from 119° to 124° C. at 0.5 mm. Hg and having a refractive index of N_d^{20} 1.4983 to 1.5003. Two groups of soap cakes were prepared according to the procedure of Example II with one group containing the stabilizer. The two groups of cakes were examined for odor and found to be identi-

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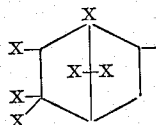
cal. They were then placed into a glass container and stored under sealed condition. After about a week the cakes were removed from the containers and upon odor examination were found to be identical. The cakes were then placed in an oven maintained at 50° C. After about 24 hours the cakes were removed from the oven, cooled to room temperature and then examined for odor loss. In all cases, the unstabilized cakes had completely lost their odor. The stabilized cakes, however, were still highly odorous and had retained their original odor in unaltered form.

I claim as my invention:

1. A method for prolonging the odor of a perfume-containing material which comprises incorporating into said material at least one compound of the formula:



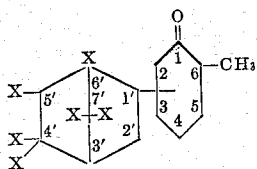
wherein n is an integer of from 1 to about 2, Y is alkyl, and R is a trimethylnorbornyl radical of the formula:



wherein X is selected from the group consisting of hydrogen and methyl, at least three X 's being methyl.

2. The method according to claim 1 wherein the perfume-containing material is a soap composition.

3. The method according to claim 2 wherein the compound incorporated into the soap composition has the formula:



wherein X is selected from the group consisting of hydrogen and methyl with three X 's being methyl.

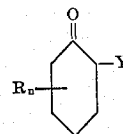
4. The method according to claim 3 wherein the compound has methyl in the 4', 4', and 5' positions.

5. The method according to claim 3 wherein the com-

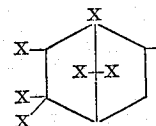
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pound is 2-(4',4',5'-trimethylnorborn-1'-yl)-6-methylcyclohexanone.

6. A perfume-containing material normally subject to loss of its odorous nature which contains at least one compound having the following formula in an amount sufficient to retard such loss:



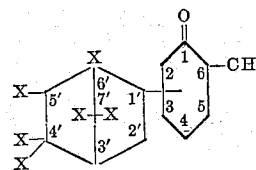
wherein n is an integer of from 1 to about 2, Y is alkyl, and R is a trimethylnorbornyl radical of the formula:



wherein X is selected from the group consisting of hydrogen and methyl, at least three X 's being methyl.

7. The perfume-containing material of claim 6 wherein said material is a soap composition.

8. The soap composition of claim 7 wherein the compound therein has the formula:



wherein X is selected from the group consisting of hydrogen and methyl with three X 's being methyl.

9. The soap composition of claim 8 wherein the compound contained therein is 2-(4',4',5'-trimethylnorborn-1'-yl)-6-methylcyclohexanone.

References Cited by the Examiner

UNITED STATES PATENTS

3,124,614 3/1964 Dankert et al. ----- 167-94 X

FOREIGN PATENTS

850,180 9/1939 France.

ALBERT T. MEYERS, *Primary Examiner*.

VERA C. CLARKE, *Assistant Examiner*.