

[54] 1,1,4,4-TETRA
METHYL-ALKYL-NITRILES-TETRAHY-
DRONAPHTHALENE PERFUME
COMPOSITIONS

3,769,348 10/1973 Wood 252/522

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[22] Filed: July 29, 1974

[21] Appl. No.: 492,521

[57] ABSTRACT

[52] U.S. Cl. 252/522; 260/465 R

[51] Int. Cl.² C11B 9/06

[58] Field of Search 252/522; 260/465 R

The 1,1,4,4-tetramethyl-alkyl-nitrile-tetrahydronaphthalenes and the perfume compositions containing them have striking odor intensities of high tenacity resembling the odors of natural musk. They do not discolor when applied as perfume material per se or when utilized in combination with other aroma chemicals in cosmetics, soaps or household products.

[56] References Cited

UNITED STATES PATENTS

2,800,511 7/1957 Carpenter et al. 252/522

3 Claims, No Drawings

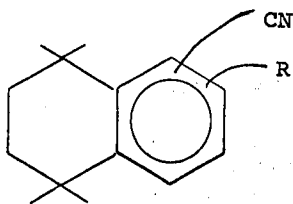
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1,1,4,4-TETRA
METHYL-ALKYL-NITRILES-TETRAHY-
DRONAPHTHALENE PERFUME COMPOSITIONS

This invention relates to 1,1,4,4-tetramethyl-alkyl-nitrile-tetrahydronaphthalenes and perfume compositions containing them.

Natural musk is derived from the Asian Musk Deer. Natural musk has two characteristic odors. One is a sweet musk odor; the other is sweaty animal odor. Strange as it may appear, both are essential for obtaining the unique musk-like odor. Natural musk is extremely expensive because of the limited quantity available. By utilization of the nitriles of this invention, both characteristics of natural musk are achieved.

In accordance with a feature of this invention, 1,1,4,4-tetramethyl-alkyl-nitrile-tetrahydronaphthalenes are utilized instead of the expensive natural musk as a perfume. The compounds of this invention are novel and have the following formula:



in which R is methyl or ethyl.

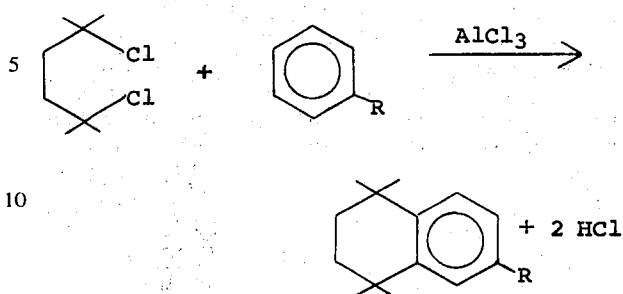
The 1,1,4,4-tetramethyl-alkyl-nitrile-tetrahydronaphthalenes of this invention have strikingly natural musk-like odors. The nitriles of this invention are several times more potent in their odor intensities than the corresponding aldehydes described in U.S. Pat. No. 2,800,511 granted on July 23, 1957 to the assignee of M. S. Carpenter et al. In addition, the odor duration of the nitriles of this invention is several times greater than that of the aldehydes. The nitriles also have a high tenacity. Besides their basic musk odor, the nitriles have very desirable by-notes. The by-note of the undiluted nitriles may be described as "mostly sweet-musty". Further, the nitriles of this invention are stable. They do not discolor when applied as perfume materials per se or when utilized in combination with other aroma chemicals in cosmetics, soaps, household products or in alcohol solutions such as perfumes or colognes. In contrast, aldehydes are relatively unstable under such conditions. They are prone to air oxidation and chemical changes are possible in alkaline or acid media.

In accordance with another feature of this invention, the novel nitriles can be advantageously utilized in the production of perfume compositions. Such compositions contain at least 1/4% by weight of the novel nitriles, and at least 1% by weight of a component which modifies the olfactory properties of the nitriles. In dilution, the nitriles exhibit a more flowery musk main-odortheme, with an animal and a slight but pleasant by-note. These characteristics are particularly manifested in the compositions containing one or both novel nitriles with other perfume compositions.

The compositions of this invention are produced, for example, by initially reacting 2,5-dimethyl-2,5-dichlorohexane with either toluene or ethylbenzene in the presence of a catalyst such as aluminum chloride.

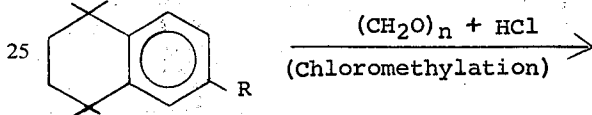
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The reaction which takes place is indicated in the following action scheme:

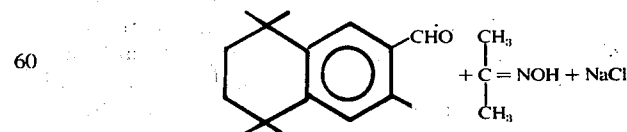
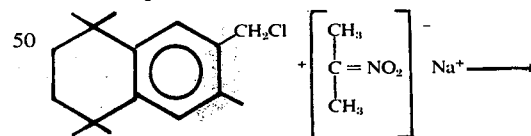


in which R is methyl or ethyl.

The resulting 1,1,4,4-tetramethyl-6-alkyl-1,2,3,4-tetrahydronaphthalene is chloromethylated with paraformaldehyde and hydrochloric acid in the presence of glacial acetic acid and phosphoric acid to produce 1,1,4,4-tetramethyl-6-alkyl-7-chloromethyl-tetrahydronaphthalene in accordance with the following reaction:

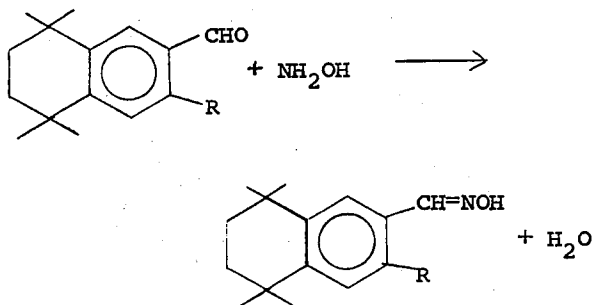


The resulting 1,1,4,4-tetramethyl-6-alkyl-7-chloromethyl-tetrahydronaphthalene is then reacted with 2-nitropropane and sodium methoxide in methanol solution. An exothermic reaction takes place. After the completion of the reaction, water and benzene are added. The resulting mixture is then separated into an organic part and an aqueous part. The organic part is washed successively with a 5% sodium hydroxide solution followed by two washings with water. The benzene is removed by distillation and the reaction product solidified. The resulting product may be recrystallized from a suitable solvent such as methanol. The reaction which takes place is as follows:

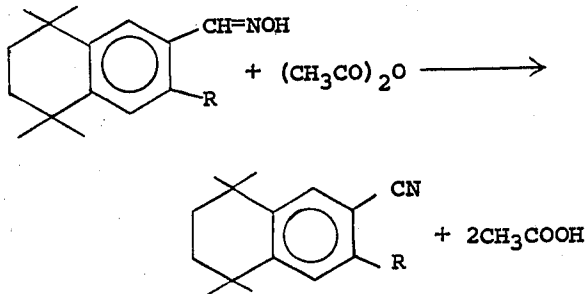


The 1,1,4,4-tetramethyl-6-alkyl-7-formyl-tetrahydronaphthalene formed is reacted with hydroxylamine hydrochloride dissolved in water. Desirably the

reaction mixture is agitated for a period of about 5 minutes, after which a solution of sodium hydroxide is added. After agitation for about 3 hours, the reaction mixture is cooled by the addition of shaved ice. The reaction mixture is then saturated with carbon dioxide by the gradual addition of solid carbon dioxide. The mixture is permitted to stand for several hours, for example overnight. The reaction which takes place is as follows:



The resulting 1,1,4,4-tetramethyl-6-alkyl-7-aldoxime tetrahydronaphthalene is reacted with acetic anhydride. The mixture is agitated and gradually heated over a period of about 15 minutes, to about 123°C . It is then refluxed for 1 hour. The reaction mixture is then permitted to cool to room temperature and a mixture of water and benzene is added. The reaction product in benzene solution is then washed successively 3 times with water, twice with aqueous sodium carbonate solution, once with aqueous sodium bicarbonate solution and finally with water. The solvent is removed by distillation and the product recrystallized by a suitable solvent such as methanol. The reaction which takes place is as follows:



A more comprehensive understanding of this invention is obtained by reference to the following examples:

EXAMPLE I

1,1,4,4,6-Pentamethyl-7-Nitrile-Tetrahydronaphthalene

To produce the starting material 1,1,4,4,6-pentamethyl-tetrahydronaphthalene, an agitated mixture of 11,056 g of toluene and 180 g of aluminum chloride, anhydrous, was cooled to 15°C and added under agitation over a period of 2 hours, keeping the temperature of the reaction mixture between 15° and 21°C , to a solution of 5000 g of toluene and 4392 g of 2,5-dimethyl-2,5-dichlorohexane. After completion of the addition, the reaction mixture was agitated at room temperature (22° – 25°C) over a period of 22 hours. The reaction mixture was then gradually heated over a per-

iod of 4 hours to 60° (maximum temperature) and then permitted to come to room temperature. To the reaction mixture was added under agitation at room temperature 6000 ml of a 5% aqueous hydrochloric acid solution. The aqueous part was separated from the organic part. The organic part was washed successively with 3000 ml of water, 3000 ml of a saturated aqueous sodium carbonate solution, 3000 ml of a saturated aqueous sodium bicarbonate solution and 3000 ml of water. The excess toluene was recovered by distillation through a 14-inch column packed with glass rings, at an ejector vacuum and the desired reaction product was obtained by fractionation at 4 mm pressure, boiling at 95° – 97°C . The yield of the 1,1,4,4,6-pentamethyl-tetrahydronaphthalene was 4228 g, (4500 ml).

1,1,4,4,6-pentamethyl-7-chloromethyl-tetrahydronaphthalene was produced by mixing in a reaction flask with agitation 1212 g of 1,1,4,4,6-pentamethyl-tetrahydronaphthalene, 440 g of paraformaldehyde, 1090 g of glacial acetic acid, 1058 g of 85% phosphoric acid and 1712 g of concentrated hydrochloric acid. The agitated reaction mixture was gradually heated over a period of 3 hours to 102°C and kept at this temperature under agitation for a period of 8 hours. There was added to the warm solution (approximately 50°C) 1500 ml of benzene and 2000 ml of water. The organic part was separated and washed successively with 1500 ml of aqueous saturated sodium carbonate solution, 1500 ml of aqueous saturated sodium bicarbonate solution and 1500 ml of water. The solvent was removed from the reaction mixture by distillation through a $\frac{1}{2}$ ft Vigreux column at an ejector vacuum. The desired 1,1,4,4,6-pentamethyl-7-chloromethyl-tetrahydronaphthalene was obtained by fractional distillation at 2 mm vacuum boiling at 128° – 130°C . The product solidified. The yield of 1,1,4,4,6-pentamethyl-7-chloromethyl-tetrahydronaphthalene was 1322 g (1300 ml) having a melting point of 78° – 81°C .

The 1,1,4,4,6-pentamethyl-7-chloromethyl-tetrahydronaphthalene is utilized to produce 1,1,4,4,6-pentamethyl-7-formyl-tetrahydronaphthalene. Initially there was dissolved 20.7 g of sodium (metal) in 300 ml of methanol. To this solution was added 101 g of 2-nitropropane at a temperature of 55°C . An exothermic reaction resulted with the temperature rising to 60°C . To the resulting reaction mixture was added 187.5 g of 1,1,4,4,6-pentamethyl-7-chloromethyl-tetrahydronaphthalene with agitation over a period of 1 hour. An exothermic reaction resulted and the reaction mixture started to reflux. The exotherm gradually subsided at 27°C after a 4-hour period of agitation. The methanol was distilled off under agitation. To the reaction mixture was added 400 ml of water and 300 ml of benzene. The mixture was separated into an organic part and an aqueous part. The organic part was washed three times with 200 ml of 5% aqueous sodium hydroxide solution, followed by two washings with 200 ml of water. The solvent, benzene, was removed by distillation and the reaction product solidified. It was recrystallized from 150 ml of methanol. The yield was 139 g with a melting point of 84° – 86°C .

The oxime of 1,1,4,4,6-pentamethyl-7-formyl-tetrahydronaphthalene was produced by initially preparing a solution of 230 g of 1,1,4,4,6-pentamethyl-7-formyl-tetrahydronaphthalene in 500 ml of 95% ethanol at a temperature of 50°C . To the 95% ethanol solution was added under agitation in one portion 82.8 g of

hydroxylamine hydrochloride dissolved in 100 ml of water. To the resulting solution of hydroxylamine hydrochloride was added under agitation during a period of about 5 minutes a solution of 60 g of sodium hydroxide in 80 ml of water. An exothermic reaction resulted, the reaction temperature rising to 72°C. After agitation for 3 hours, the temperature of the reaction mixture declined to 28°C. To cool the mixture, 500 g of shaved ice was added. The temperature of the reaction mixture dropped to -2°C. The reaction mixture was then saturated with carbon dioxide by the gradual addition of 250 g of dry ice. The reaction mixture decreased to -15°C during a 10 minute period. It then rose gradually to 15°C during the following 3 hours. It was then permitted to stand overnight. The solid oxime (aldoxime) was collected on a Buchner funnel and washed 4 times with 100 ml of water followed by two washings with 100 ml of hexane. The yield was 240 g of 1,1,4,4,6-pentamethyl-7-aldoxime-tetrahydronaphthalene having a melting point of 148°-140°C.

To produce the corresponding nitrile, 200 g of 1,1,4,4,6-pentamethyl-7-aldoxime-tetrahydronaphthalene were mixed with 200 g of acetic anhydride. The mixture was agitated and gradually heated over a period of 15 minutes to 120°C. The reaction mixture was then refluxed for 1 hour, and then permitted to come to room temperature. There were added 400 ml of water and 300 ml of benzene. The organic part was then washed 3 times with 150 ml of water followed by twice washing with 150 ml of aqueous sodium carbonate solution, followed by one washing with 150 ml of aqueous sodium bicarbonate solution and finally with 150 ml of water. The solvent, benzene, was removed by distillation. The product solidified. There were obtained 176 g of the crude product. The product was recrystallized from methanol. A yield of 145 g of 1,1,4,4,6-pentamethyl-7-nitrile-tetrahydronaphthalene having a melting point of 124°-125°C was obtained.

EXAMPLE II

1,1,4,4,-Tetramethyl-6-Ethyl-7-Nitrile-Tetrahydronaphthalene

To produce the starting material 1,1,4,4-tetramethyl-6-ethyl-tetrahydronaphthalene, an agitated mixture of 1484 g of ethylbenzene and 30 g of ferric chloride was added under cooling, keeping the reaction mixture at -5°C over a period of one hour, a solution of 732 g of 2,5-dimethyl-2,5-dichlorohexane and 1272 g of ethyl benzene. After completion of the addition, agitation was continued at -4°C over a period of 3 hours. The reaction mixture was poured over 1400 g of ice containing 60 g of concentrated hydrochloric acid. The organic part was separated from the aqueous part and the organic part was washed twice with 500 ml of water followed by a single washing successively with 500 ml of saturated sodium carbonate solution, 500 ml of saturated sodium bicarbonate solution and 500 ml of water. The unreacted excess ethylbenzene was recovered by fractionation from a steam bath and an ejector vacuum through a 14 inch column, packed with glass rings. The reaction product was fractionated at 1-1.5 mm pressure boiling at 83°-86°C. The yield was 754 g of 1,1,4,4-tetramethyl-6-ethyl-tetrahydronaphthalene.

1,1,4,4-tetramethyl-6-ethyl-7-chloromethyl-tetrahydronaphthalene was then produced by adding to a reaction flask and agitating the following:

648 g of 1,1,4,4-tetramethyl-6-ethyl-tetrahydronaphthalene

220 g of paraformaldehyde

545 g of glacial acetic acid

336 g of 85% phosphoric acid

856 g of concentrated hydrochloric acid.

The reaction mixture was heated to 98°-100°C over a period of 24 hours. The G. L. C. examination indicated that 80% had reacted. Hydrogen chloride gas was then introduced into the reaction mixture at 68°-70°C for 1½ hours. The reaction mixture was then permitted to cool and 1500 ml of water and 750 ml of hexane were added. The reaction mixture was agitated for 10 minutes, permitted to set and separated into an organic part and an aqueous part. The organic part was washed twice with 500 ml of water followed by a single washing in 500 ml of saturated sodium carbonate solution, 500 ml of saturated sodium bicarbonate solution and 500 ml of water. The solvent, hexane, was removed by distillation under an ejector vacuum. The reaction product was fractionated through a ½ foot Vigreux column at a 1 mm vacuum, boiling at 117°-119°C. It solidified. The yield was 618 g of 1,1,4,4-tetramethyl-6-ethyl-7-chloromethyl-tetrahydronaphthalene having a melting point of 66°C.

The 1,1,4,4-tetramethyl-6-methyl-7-chloromethyl-tetrahydronaphthalene is utilized to produce 1,1,4,4-tetramethyl-6-ethyl-7-formyl-tetrahydronaphthalene. Initially, 57.5 g of sodium (metal) were dissolved in 800 ml of methanol. An exothermic reaction resulted. To this solution was added at a temperature of 55°C 267 g of 2-nitropropane. An exothermic reaction resulted with the temperature rising to 65°C. There were then added under agitation over a period of 15 minutes 528 g of 1,1,4,4-tetramethyl-6-ethyl-7-chloromethyl-tetrahydronaphthalene. The temperature rose to 70°C under reflux. Continued agitation and heat were applied to reflux at 70°C. The methanol was removed by distillation under agitation. To the crude reaction product was added 1000 ml of water and 500 ml of hexane. The mixture was agitated for 5 minutes and the aqueous part and the organic part were separated. The organic part was successively washed with 500 ml of water, 500 ml of a 5% sodium hydroxide aqueous solution, 500 ml of a saturated sodium bicarbonate aqueous solution, and 500 ml of water. The solvent, hexane, was removed by distillation through a ½ ft Vigreux column at 1 mm pressure. The yield of 1,1,4,4-tetramethyl-6-ethyl-7-formyl-tetrahydronaphthalene was 443 g which had a boiling point of 120°C.

The oxime of 1,1,4,4-tetramethyl-6-ethyl-7-formyl-tetrahydronaphthalene was produced by initially dissolving 48.8 g of 1,1,4,4-tetramethyl-6-ethyl-7-formyl-tetrahydronaphthalene in 100 ml of 95% ethanol. The solution was warmed to 50°C under agitation until the solution was clear. To the clear ethanol solution was added, over a period of 15 minutes at 50°C 16.7 g of hydroxylamine hydrochloride dissolved in 20 ml of water. To the resulting mixture was added, over a period of 5 minutes at a temperature of 44°C, a solution of 12 g of sodium hydroxide dissolved in 16 ml of water. The reaction being exothermic, the reaction temperature rose to 56°C and then declined. The reaction mixture was agitated for 3½ hours. The temperature of the reaction mixture declined to 25°C. 100 g of shaved ice was added, the reaction temperature dropping to -2°C. 50 g of solid carbon dioxide (dry ice) in small pieces were

added. The reaction temperature dropped to -15°C , then gradually increased to 23°C during agitation over 2 1/4 hours. Agitation was terminated and the reaction mixture was permitted to stand overnight. The formed crystals were filtered off on a Buchner funnel. The crystals were washed with 50 ml water portions until neutral to litmus. The yield was 50 g of 1,1,4,4-tetramethyl-6-ethyl-7-aldoxime-tetrahydronaphthalene having a melting point of $135^{\circ}\text{--}137^{\circ}\text{C}$.

To produce 1,1,4,4-tetramethyl-6-ethyl-7-nitrile-tetrahydronaphthalene, 48.2 g of 1,1,4,4-tetramethyl-6-ethyl-7-aldoxime-tetrahydronaphthalene were mixed with 50 g of acetic anhydride. The mixture was heated over a period of 15 minutes to reflux at 140°C and the reflux continued for one half hour. The reaction mixture was poured over 120 ml of ice and water. It was agitated and 100 ml of hexane were added. The mixture was separated into an organic part and an aqueous part. The organic part was washed with 100 ml of warm water, then agitated for 20 minutes with 200 ml of a 5% sodium bicarbonate solution. The organic part and aqueous part were then separated. The organic part was washed twice with 50 ml of water. It was neutral to litmus. The solvent was removed by distillation. The reaction product was fractionated through a 6-inch Vigreux column. The yield of 1,1,4,4-tetramethyl-6-ethyl-7-nitrile-tetrahydronaphthalene was 32.5 g having a boiling point at $110^{\circ}\text{--}112^{\circ}\text{C}$ at 0.4 mm. The product solidified and had a melting point of $40^{\circ}\text{--}40.5^{\circ}\text{C}$.

EXAMPLE III

Ambrone Perfume Composition

An Ambrone perfume composition is prepared by mixing together the following:

| | |
|-------------|---|
| 120 parts | Oil Mandarin Italian |
| 150 parts | Oil Bergamot Natural |
| 115 parts | Resinoid Labdanum |
| 100 parts | Isobutyl Benzoate |
| 80 parts | Tincture Civet |
| 80 parts | Jasmine Synthetic |
| 85 parts | Rose Synthetic |
| 35 parts | Oil Patchouly Singapore |
| 30 parts | Tincture Castoreum |
| 30 parts | Oil Vetivert Bourbon |
| 30 parts | 1,1,4,4-Tetramethyl-6-Ethyl-7-Nitrile-Tetrahydronaphthalene |
| 15 parts | Musk Ambrette |
| 20 parts | Coumarin |
| 110 parts | Heliotropin |
| 1,000 parts | |

EXAMPLE IV

Rose Perfume Composition

A rose perfume composition is prepared by mixing together the following:

| | |
|-------------|---|
| 450 parts | Rhodinol |
| 90 parts | Rose Geranium Oil, Terpeneless |
| 50 parts | Aldehyde C ₁₁ |
| 10 parts | Citral |
| 5 parts | 1,1,4,4-Tetramethyl-6-Ethyl-7-Nitrile-Tetrahydronaphthalene |
| 5 parts | 1,1,4,4,6-Pentamethyl-7-Nitrile-Tetrahydronaphthalene |
| 5 parts | Musk Ketone |
| 20 parts | Cinnamic Alcohol |
| 200 parts | Rose Absolute |
| 165 parts | Phenylethyl Propionate |
| 1,000 parts | |

EXAMPLE V

Lavender Perfume Composition

A Lavender perfume composition is prepared by mixing together the following:

| | |
|-------------|---|
| 20 parts | Oleoresin Orris Root - Florentine - Food Grade |
| 25 parts | Oil Thyme White N.F. Extra |
| 30 parts | Oil Patchouly Singapore |
| 30 parts | Borneol |
| 40 parts | 50% solution Oak Moss Absolute |
| 40 parts | Heliotropin |
| 50 parts | Oil Geranium Algerian Extra |
| 30 parts | 1,1,4,4-Tetramethyl-6-Ethyl-7-Nitrile-Tetrahydronaphthalene |
| 30 parts | Musk Tibetan |
| 75 parts | Oil Rosemary Extra |
| 200 parts | Oil Bergamot Natural |
| 430 parts | Oil Lavender |
| 1,000 parts | |

EXAMPLE VI

Musk Perfume Composition

A Musk perfume composition is prepared by mixing together the following:

| | |
|-------------|---|
| 100 parts | Geranium Oil Algerian |
| 100 parts | Clove oil |
| 30 parts | Cassia Oil |
| 20 parts | Labdanum Oleo-Resin |
| 50 parts | Castoreum Tincture |
| 50 parts | Sandalwood Oil |
| 150 parts | Cedarwood Oil |
| 30 parts | α -Ionone |
| 30 parts | Vetivert Oil |
| 100 parts | 1,1,4,4-Tetramethyl-6-Ethyl-7-Nitrile-Tetrahydronaphthalene |
| 50 parts | 1,1,4,4,6-Pentamethyl-7-Nitrile-Tetrahydronaphthalene |
| 40 parts | Musk Xylene |
| 100 parts | Benzyl Benzoate |
| 150 parts | α -Terpineol |
| 1,000 parts | |

EXAMPLE VII

Sachet Powder

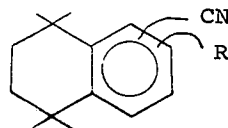
A sachet powder containing no perfume component other than one or a mixture of two novel nitrile tetrahydronaphthalenes of this invention may be prepared by mixing intimately:

50 parts of one or a mixture of two novel nitrile tetrahydronaphthalenes with:

50 parts of talcum powder or kaolin or any diatomaceous earth.

What is claimed is:

1. A composition for use in perfumes comprising at least 1/4 % by weight of a tetramethyl-alkyl-nitrile-tetrahydronaphthalene and at least 1% by weight of a component which modifies the olfactory properties of said compound, said tetramethylalkyl-nitrile-tetrahydronaphthalene having the formula:



in which R is methyl or ethyl.

2. A composition in accordance with claim 1 in which the compound is 1,1,4,4,6-pentamethyl-7-nitrile-tetrahydronaphthalene.

3. A composition in accordance with claim 1 in which the compound is 1,1,4,4-tetramethyl-6-ethyl-7-nitrile-tetrahydronaphthalene.

* * * * *

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,910,853 Dated October 7, 1975

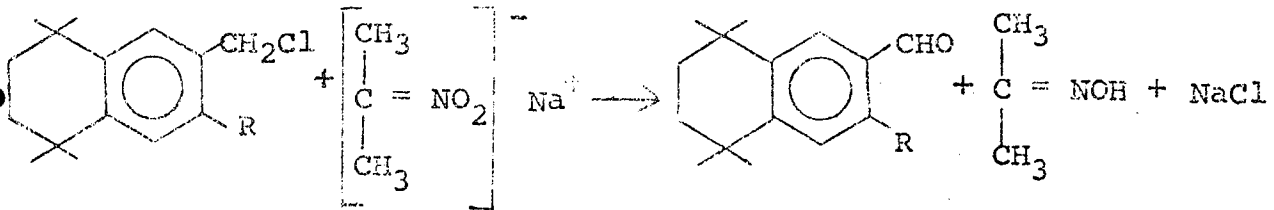
Inventor(s) Kurt Kulka

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

The title of the invention on the first page and in Column 1 should read as follows:

1,1,4,4-TETRAMETHYL-ALKYL-NITRILE-TETRAHYDRONAPHTHALENE
PERFUME COMPOSITIONS

Column 2, lines 48-65, the formula should read as shown below:



Column 5, line 21, "140°" should read ---150°---

Column 6, line 30, correct the spelling of "exothermic".

Column 7, line 28, insert a degree sign after "112".

Signed and Sealed this

twenty-third Day of March 1976

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks