

United States Patent

Lamberti et al.

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[54] **DETERGENT COMPOSITIONS
CONTAINING THE ETHERS AND
ESTERS OF TETRAHYDROFURAN AND
TETRAHYDROPYRAN**

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[63] Continuation-in-part of Ser. No. 763,374, Sept. 27,
1968, abandoned.

[52] U.S. Cl. **252/89, 252/522**

[51] Int. Cl. **C11d 1/00**

[58] Field of Search **252/89, 522; 167/94;
260/345.9, 347.8**

[56]

References Cited

UNITED STATES PATENTS

2,356,903	8/1944	Wood	252/550
3,275,561	9/1966	Pye et al.	252/110
3,227,731	1/1966	Kulka	252/522
3,252,998	5/1966	Ohloff et al.	252/522
3,470,209	9/1969	Lombarsky	260/347.8

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[57]

ABSTRACT

Detergent compositions containing an organic detergent and,
as a perfumery ingredient, an ester or ether of tetrahydrofuran
or tetrahydropyran.

11 Claims, No Drawings

DETERGENT COMPOSITIONS CONTAINING THE ETHERS AND ESTERS OF TETRAHYDROFURAN AND TETRAHYDROPYRAN

This application is a continuation-in-part of my copending U.S. application, Ser. No. 763,374, filed Sept. 27, 1968 now abandoned.

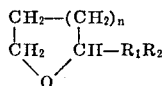
In the manufacture of cleansing compositions containing detergents, it has been found necessary to incorporate materials having pleasant fragrances in order to mask undesirable odors in the detergent compositions so as to increase consumer acceptance of the products. The well-known fragrant materials of the ester class, such as benzyl acetate and benzyl propionate, are examples of such additives. However, since most detergent formulations contain alkali, perfumery materials, such as the aforementioned esters, are decomposed by hydrolysis either during storage or during use in aqueous solutions.

A further problem which has arisen in the use of perfumery materials and cleansing compositions concerns the presence of bleaching ingredients. The latter materials tend to oxidize perfumery additives and it has been found that the perfumes are decomposed upon storage in the presence of many bleaching ingredients.

It is an object of this invention to provide detergent compositions having desirable fragrances and are not discolored.

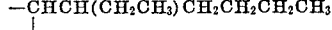
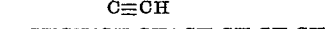
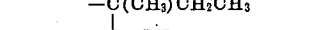
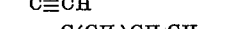
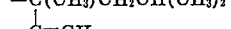
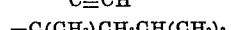
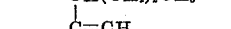
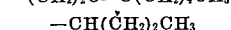
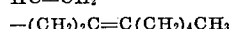
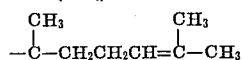
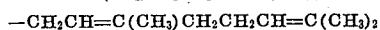
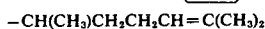
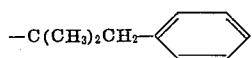
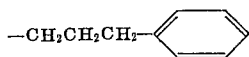
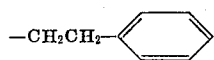
A further object is the production of detergent compositions with desirable odor characteristics which retain their fragrances in the presence of bleaching ingredients and which are stable in alkaline media.

The perfumery compounds used in the detergent compositions of the invention are the ethers and esters of tetrahydrofuran and tetrahydropyran having the structural formula



wherein n is 1 or 2, R_1 is either $-\text{O}-$ or $\text{CH}_2\text{O}-$ and R_2 is one of the following alkyl, aralkyl, alkenyl, alkynyl or alkylcarbonyl radicals:

C_3 to C_{11} alkyl (propyl, butyl, amyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl)



The amyl tetrahydropyran ether has a lavender odor, the isoamyl tetrahydropyran ether has a soft lavender odor, the hexyl tetrahydropyran ether has a witch hazel character and the decyl tetrahydropyran ether has a clean, soapy odor. The odors of the remaining twelve non-alkyl tetrahydropyran compounds given above are respectively green, rose-slightly sharp; flowery, slightly sharp green; green, floral as apple blossom; green, linden-like, strong; green rosy, more leafy than geraniol; fragrant, lily-linden, fresh; violet leaf green, similar to methyl heptyne carbonate; strong bitter earthy, slight green galbanum type; animal-civet like, strong; fresh, ethereal, earthy, strong; high-pitched, waxy violet; and clean, rosy green, spicy.

The tetrahydrofuran compounds have nearly the same odor as the tetrahydropyran compounds described above except for the following: n-hexyloxytetrahydrofuran has a natural green odor; n-heptyloxytetrahydrofuran has a fresh green jasmine odor; n-octyloxytetrahydrofuran has an intense citrus note; 2-pentyloxymethyltetrahydrofuran has a sweet, floral odor; 2-decyloxytetrahydrofuran has a clean, citrus-like odor; the 2-nonyloxytetrahydrofuran has a rosy odor; and the tetrahydrofuran ether of Formula 7 has a Bois de rose odor.

The tetrahydropyran and tetrahydrofuran ethers or esters may be prepared in the conventional or classical manner by reacting dihydropyran or dihydrofuran with the appropriate alcohol or carboxylic acid corresponding to the R_2 radical above. Thus the appropriate alcohol for the compound of Formula II is phenylethanol while the appropriate alcohol for the compound of Formula VII is linalool. For example, dihydropyran or dihydrofuran (0.6 mole) and the appropriate alcohol or carboxylic acid (0.5 mole) are stirred for one hour with a catalytic amount of p-toluene sulfonic acid. The mixture is cooled, taken up in ether, washed with sodium hydroxide solution and then with water until neutral. The ether layer is dried over anhydrous magnesium sulfate and concentrated on a steam bath (with a stream of air blowing on the mixture). The structures of the dihydropyran or dihydrofuran adducts are confirmed by NMR (nuclear magnetic resonance) analysis. More specifically, for example the compound 2-decyloxytetrahydrofuran is prepared as follows:

A mixture of 2,3-dihydrofuran, 4.2 g (0.06 mole) prepared by the method of Paule et al. [Bull. Soc. Chim. France 668 (1950)] 7.9 g (0.05 mole) and a spatula full of p-toluenesulphonic acid was stirred for one hour. The reaction mixture was the cooled, taken up in ether, washed with water until neutral. The ether layer was dried over anhydrous MgSO_4 , filtered and concentrated under vacuum at 40°C until all traces of ether and excess 2,3-dihydrofuran had disappeared. The residue, 2-decyloxytetrahydrofuran, has a very clean, citrus-like odor.

To form the compounds where R_1 is $\text{CH}_2\text{O}-$ the following procedures are used:

Tetrahydropyran-2-methanol, 35 g (0.3 mole) was dissolved in 80 ml of benzene and reacted with 7 g (0.3 mole) of metallic sodium at refluxing temperature for eight hours. n-Hexyl bromide, 50 g (0.3 mole) was then added and the reaction mixture refluxed for three more hours. The reaction mixture was then filtered to remove sodium bromide, concentrated in vacuo, and the residue distilled to yield 26.1 g of the desired 2-hexyloxymethyltetrahydropyran, b.p. $144^\circ\text{--}146^\circ\text{C}/33\text{ mm.}$, which has a powerful, green stem, ivy-like odor.

Using the procedure for preparing 2-hexyloxymethyltetrahydropyran 1, 31 g (0.3 mole) of tetrahydrofurfuryl alcohol, 7 g of sodium and 45 g (0.3 mole) of n-pentyl bromide were reacted to product 19.6 g of the desired 2-pentyloxymethyltetrahydrofuran, b.p. $116^\circ\text{--}118^\circ\text{C}/30\text{ mm.}$, which has a sweet, floral odor.

The detergent compositions of the invention may take any desired physical form, such as liquids, pastes, flakes, beads, powders, bars, tablets and the like. The compositions may be either heavy-duty or light-duty formulations and can be prepared in the conventional manner.

The detergent compositions contain conventional amounts, such as 5 to 99 percent by weight of an organic detergent and from about 0.01 to about 2 percent weight of the dihydropyran ether or ester. The organic detergent component can be soap, i.e., a salt of a higher fatty acid and/or a non-soap organic detergent including the anionic, cationic, nonionic, ampholytic, and zwitterionic detergent compounds. These organic detergent materials are well known and the chemical nature thereof is not a feature of the invention. Typical suitable organic detergents are set forth in "Surface Active Agents" by Schwartz and Perry and "Surface Active Agents and Detergents" by Schwartz, Perry and Berch, the disclosures of which are incorporated by reference herein.

The detergent compositions can contain conventional compounding materials in the usual amounts therefor, such as chlorine releasing bleaching agents, typical examples of which include chlorocyanurates, chlorinated trisodium phosphate, N-chlorosuccinimide, calcium hypochlorite, and N,N-dichloroazocarbonamidine; alkali, such as sodium hydroxide, potassium hydroxide, sodium carbonate, and the like; builders, typical examples of which are pentasodium and pentapotassium triphosphosphate, tetrasodium and tetrapotassium pyrophosphate, trisodium nitrilotriacetate, and the like; sequestrants such as ethylene diamine tetraacetic acid and the like; soil suspending agents, for example, sodium carboxymethylcellulose and the like; fillers, representative examples of which include sodium carbonate, sodium sulfate and the like; suds boosters, such as lauric diethanolamide and the like; suds depressants, for example, long-chain monohydric alcohols; germicides, representative examples of which include 3,4',5-tribromosalicylanilide, hexachlorophene and the like; colorants; abrasives; enzymes; etc.

Although the ethers and esters of tetrahydropyran and tetrahydrofuran can be used as the sole perfumery ingredient for detergent compositions, they are more usually used, as is the custom, in a perfumery blend therefor. Representative examples of such perfume blends for detergent compositions are set forth in the following examples.

EXAMPLE 1

Components	Parts by Weight
Benzyl Acetate	40
Cinnamic Alcohol	180
Dimethyl Benzyl Carbinol	50
Hydroxycitronellal	30
Ionone Ketone	70
Linalool	100
Compound of Formula II above wherein n is 2 and R_1 is —O—	30
Phenyl Ethyl Acetate	65
Phenyl Ethyl Alcohol	150
Styrax Resin	100
Total	815

EXAMPLE 2

Components	Parts by Weight
Amyl Salicylate	200
Anisic Aldehyde	30
Benzyl Acetate	60
Compound of Formula XII above wherein n is 2 and R_1 is —O—	40
Coumarin	40
Dimethyl Hydroquinone	50
Methyl Ionone Gamma	35
Musk Ambrette	10
Musk Xylol	40
Styrax Resin	10
Terpineol	50
Ylang Synthetic	30
Total	595

EXAMPLE 3

Components	Parts by Weight
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Alpha Methyl Cinnamic Aldehyde	7
Coumarin	40
Compound of Formula I above wherein R_2 is hexyl, R_1 is —O— and n is 2	155
Linalool	450
Linalyl Acetate	220
Petitgrain	10
Rosemary	5
Total	913

EXAMPLE 4

Components	Parts by Weight
Camphor	50
Eucalyptol	50
Linalool	100
Linalyl Acetate	100
Compound of Formula VII above wherein n is 2 and R_1 is —O—	200
3-Nonanone	100
Petitgrain	100
Total	700

EXAMPLES 5-7

The components of Example 1 except in place of the compound of Formula II wherein n is 2 and R_1 is —O—, the following materials are used: 2-hexyloxymethyltetrahydropyran, 2-pentyloxymethyltetrahydropyran, and 2-decyloxymethyltetrahydropyran.

EXAMPLES 8-10

The same components of Example 2 except in place of the compounds of Formula XII wherein n is 2 and R_1 is —O—, the following compounds are used: 2-octyloxytetrahydrofuran, 2-decyloxytetrahydrofuran, and 2-linalyloxytetrahydrofuran.

The alkali stability and chlorine stability of the perfumed detergent compositions of the invention are illustrated by the following examples:

EXAMPLE 11

Eight dishwasher products are provided with 0.1 percent by weight of each of the respective tetrahydropyran ethers R_1 = —O— having Formulas I (R_2 is hexyl), II, VII, XII above and tetrahydrofuran ethers R_1 = —O— (R_2 is hexyl), II, VII, XII above and the ingredients shown hereinbelow:

Ingredients	Parts by Weight
Pentasodium triphosphate ¹	44.00
Chlorinated Trisodium phosphate ¹	9.60
N-silicate ¹	7.414
RU-silicate ¹	5.878
Nonionic Detergent (Pluronic L62)	2.25
Nonionic Detergent (Pluronic L61)	0.75
Colorants	0.004
Water	30.104
Total	100.00

¹Expressed on dry basis.

After storage for 6 days at 95° F in both closed jars and commercial packages, these eight formulations lost none of their perfume odor.

EXAMPLE 12

Eight liquid detergent formulations were perfumed with 0.1 percent by weight of each of the respective tetrahydropyran

ethers $R_1 = -O-$ having Formulas I (R_2 is hexyl), II, VII, XII above and tetrahydrofuran ethers R_1 is $-CH_2O-$ having Formulas I (R_2 is hexyl), II, VII, and XII above.

Ingredients	Parts by Weight
Potassium dodecylbenzene sulfonate	10
Sodium xylene sulfonate	8
Lauric/myristic diethanolamide	2.7
Lauric/myristic isopropanolamide	3.0
Potassium pyrophosphate	18.0
Sodium silicate	2.5
Sodium carboxymethyl cellulose	0.15
Methyl cellulose	0.57
Water	(to 100%)

The perfume odors of these eight formulations were unaffected after being stored in accordance with the procedure described in Example 11.

EXAMPLE 13

Four scouring cleanser-type formulations indicated below were perfumed with 0.1 percent by weight of each of the respective tetrahydropyran ethers having the Formulas I (R_2 is hexyl), II, VII and XII above.

Ingredients	Parts by Weight
Silica, 90 mesh	70
Chlorinated trisodium phosphate	10
Sodium alkylbenzene sulfonate	3.33
Sodium tripolyphosphate	16.67
Total	100.00

After storage, as per Example 11, the perfume odors of these four formulations were unaffected.

Comparable storage stability was achieved with the other tetrahydropyran and tetrahydrofuran ethers and esters given above.

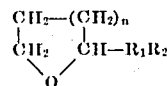
All the tetrahydropyran and tetrahydrofuran ethers and esters also passed the following soap bar stability test. The perfumery material is incorporated at the 1 percent level (or the 0.5 percent level if the odor is very intense as is the case for some of the acetylenic tetra-hydropyran ethers) in an 80-20 percent tallow-coconut soap base. The perfumed soap chips are extruded and cut into minirectangular bars (about 45 grams each). The bars are enclosed in foil-laminated white cartons and aged at room temperature for 2-4 weeks. The bars are then rated for odor intensity, odor quality and any discoloration that may have taken place. Perfumery materials which satisfactorily cover the normal soapy base odor without causing significant discoloration of the bars are judged useful for incorporation in soap bar perfumes as well as in perfumes for use in alkaline detergent products.

The detergent compositions of the invention are thus provided with perfumery materials which are unaffected in their stability toward alkali or chlorine releasing bleach agents, which stability properties are not possessed by many present day perfumery materials. Any undesirable odors present in the detergent compositions of the invention are thus masked by the pleasant fragrances or notes of the tetrahydropyran and tetrahydrofuran ether and ester perfumery ingredients. Moreover, the tetrahydropyran and tetrahydrofuran ether and ester perfumery ingredients can be very readily prepared by simple conventional chemical means and at a relatively inexpensive cost.

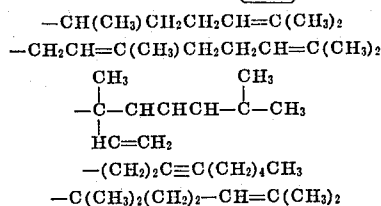
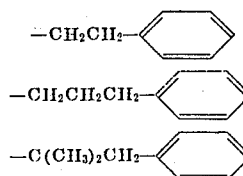
It will be appreciated that various modifications and changes can be made in the products of the invention by those skilled in the art without departing from the essence of the invention and that accordingly the invention is to be limited only within the scope of the appended claims.

What is claimed is:

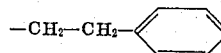
1. A detergent composition consisting essentially of an organic detergent "selected from the group consisting of soap, anionic, cationic, nonionic ampholytic and zwitterionic detergent compounds" and from about 0.01 to about 2 percent by weight, of a perfumery ingredient, having the structural formula:



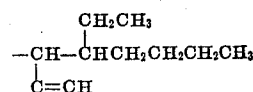
wherein n is 1 or 2, R is selected from the group consisting of $-O-$ and $-CH_2O-$ and R_2 is selected from the group consisting of C_3 to C_{11} alkyl



2. The detergent composition as defined by claim 1 wherein n is 2, R_1 is $-O-$ and the R_2 radical is

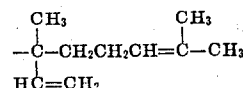


3. The detergent composition as defined by claim 1 wherein n is 2, R_1 is $-O-$ and the R_2 radical is



4. The detergent composition as defined by claim 1 wherein n is 2, R_1 is $-O-$ and the R_2 radical is $-(\text{CH}_2)_5\text{CH}_3$

5. The detergent composition as defined by claim 1 wherein n is 2, R_1 is $-O-$ and the R_2 radical is

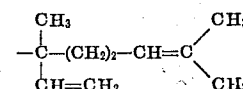


6. The detergent composition as defined by claim 1 wherein n is 1, R_1 is $-O-$ and the R_2 radical is C_8H_{13} .

7. The detergent composition as defined by claim 1 wherein n is 1, R_1 is $-O-$ and the R_2 radical is C_8H_{17} .

8. The detergent composition as defined by claim 1 wherein n is 2, R_1 is $-O-$ and the R_2 radical is $C_{10}H_{21}$.

9. The detergent composition as defined by claim 1 wherein n is 1, R_1 is $-O-$ and the R_2 radical is



10. The detergent composition as defined by claim 1 wherein n is 2, R_1 is $-CH_2O-$ and the R_2 radical is C_6H_{13} .

11. The detergent composition as defined by claim 1 wherein n is 1, R_1 is $-CH_2O-$ and the R_2 radical $-C_5H_{11}$.

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