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DETERGENT COMPOSITION

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6 Claims. (Cl. 252—132)

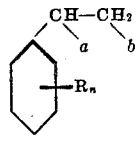
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This invention is concerned with new compositions of matter.

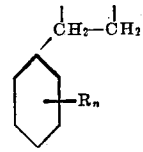
More particularly, this invention relates to new compositions of matter comprising a soap or detergent containing one or more esters of alkyl phenyl ethyl alcohols as perfuming and/or sealing agents.

An object of the present invention is the provision of a stable perfuming and/or sealing agent for soaps and detergents in general comprising one or more esters of alkyl phenyl ethyl alcohols. Another object of the invention is the provision of a method whereby bar or cake soap may be effectively sealed against the loss of moisture, and consequent deterioration, by the addition thereto of one or more esters of alkyl phenyl ethyl alcohols. A further object of the invention is the provision of new perfuming agents for soap possessing unusually stable characteristics. Other objects and advantages of the invention will be apparent to those skilled in the art upon an inspection of the specification and claims.

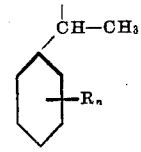
Esters of alkyl phenyl ethyl alcohols are stable organic compounds having unusually desirable odors. Their structure may be represented as follows.



in which one of the group consisting of *a* and *b* is an —OOCX group, in which X is hydrogen, alkyl, alkenyl, substituted alkyl, substituted alkenyl, aryl, substituted aryl, alkyl-aryl, substituted alkyl-aryl, aryl-alkyl, substituted aryl-alkyl, the



group, or the



group, the remaining group is hydrogen, R_n represents from one to five nuclearly substituted alkyl groups.

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Esters of alkyl phenyl ethyl alcohols may be prepared by reacting such alcohols with one or more acids selected from a list comprising formic, acetic, propionic, butyric, valeric, caproic, oenanthic, caprylic, pelargonic, capric, and similar acids having a higher number of carbon atoms; unsaturated acids such as acrylic acid, methacrylic acid, crotonic acid, isocrotonic acid, vinylacetic acid, and the like; halogenated fatty acids such as chloroformic acid, monochloracetic acid, dichloroacetic acid, alpha-chloropropionic acid, and the like; hydroxy acids, glycollic acid, lactic acid, alpha-hydroxylbutyric acid, and the like; amino acids, such as glycine, alanine, valine, leucine, and the like; dibasic acids, such as oxalic acid, malonic acid, methyl malonic acid, succinic acid, maleic acid, fumaric acid, and the like; aromatic carboxylic acids, such as benzoic acid, anthranilic acid, salicylic acid, phthalic acid, and the like; and aryl-substituted aliphatic acids, such as phenyl acetic acid, hydrocinnamic acid, phenyl propionic acid, cinnamic acid, and the like.

I have discovered that such esters are particularly desirable sealing and perfuming agents for soaps and detergents.

Especially desirable results are obtained when esters of tolylethyl alcohols are employed as sealing and perfuming agents for soaps and detergents. The use of alkyl esters of such alcohols has been found to be particularly advantageous.

The preparation of alpha tolylethyl alcohols is disclosed and claimed in my copending application, Serial Number 290,501, filed August 16, 1939, now Patent 2,293,774, issued August 25, 1942.

The use of acetic, propionic, butyric, and valeric acid esters of tolylethyl alcohols, and particularly the use of such esters of mixed tolylethyl alcohols containing m-tolylethyl alcohol, p-tolylethyl alcohol, and o-tolylethyl alcohol, in which such alcohols are present in the mixture in decreasing proportions as listed, will be found particularly advantageous.

Esters of tolylethyl alcohols containing from 50 to 75% of the meta form, from 20 to 50% of the para form, and from 1 to 10% of the ortho form possess very desirable odors. Particularly desirable results are obtained when mixtures of tolylethyl alcohol esters containing from 60 to 70% of the meta form, from 25 to 40% of the para form, and from 2 to 8% of the ortho form are employed. These preferred mixtures may be obtained readily by a proper adjustment of the boiling range of the light oil methyl styrene fractions

employed in the production of the mixed alcohols, which then may be esterified.

The preparation of the acetic, propionic, butyric, and valeric acid esters of tolylethyl alcohols are disclosed and claimed in my copending applications, Serial Nos. 290,502, filed August 16, 1939, now Patent 2,293,775, issued August 25, 1942; 417,315, filed October 31, 1941; 313,342, filed January 11, 1940; and 417,316, filed October 31, 1941, respectively.

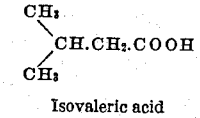
Such esters may be prepared by the reaction of the desired tolylethyl alcohol, or mixture of tolylethyl alcohols, or derivatives of tolylethyl alcohols containing an atom or group capable of being replaced with an ester group corresponding to the desired acid or mixture of acids with the desired acid or anhydride, or salts or derivatives thereof.

The preparation of such esters may be illustrated by the preparation of the valeric acid esters of tolylethyl alcohols.

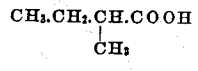
Valeric acid occurs in four isomeric forms, as follows.

$CH_3.CH_2.CH_2.CH_2.COOH$

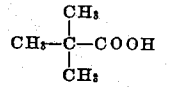
n-Valeric acid



Isovaleric acid



Active valeric acid



Pivalic acid

The conversion of tolylethyl derivatives to tolylethyl esters of valeric acids may be carried out in any suitable manner, and with any suitable esterification apparatus.

Any suitable esterification reagent, such as a valeric acid, its anhydride, its salt or mixtures thereof, may be employed as desired.

For example, valeric acid or acid halides thereof may be employed for the conversion of tolylethyl alcohols or metallic derivatives thereof to valerates, and salts of valeric acid may be used for the conversion of tolylethyl halides to valerates.

Illustrative of the salts of valeric acid which may be employed as esterification reagents may be mentioned sodium valerate, potassium valerate, calcium valerate, iron valerate, lead valerate and other salts. These salts may be the normal valerates, or the isomeric valerates, or any desired mixture thereof.

The esterification reaction may be carried out in the presence of a solvent, such as for example, benzene, if desired.

Any suitable reaction temperature may be employed, such as for example, the boiling point of the solution.

The esterification reaction may be carried out at atmospheric, subatmospheric, or superatmospreric pressures, as desired.

Suitable esterification catalysts, such as, for example, sulfuric acid, phosphoric acid or anhydrous hydrogen chloride, may be advantageously employed in certain of the reactions, particularly in the conversion of tolylethyl alcohols to esters of valeric acids.

The use of a system whereby any water formed by the esterification reaction can be continuously removed from the system will, in general, be found advantageous from the standpoint of the yield of ester secured, as well as from the standpoint of the considerable reduction in time necessary to complete the reaction.

One suitable method for effecting the esterification processes of the present invention comprises refluxing the derivatives with esterification reagents for a period of several hours.

For example, salts of valeric acids may be refluxed with tolylethyl halides to produce the corresponding tolylethyl esters. This reaction may, if desired, be effected in the presence of the corresponding valeric acid.

The tolylethyl esters thus produced may be suitably separated from the halogen salts in the reaction mixture, for example, by filtration.

If a valeric acid has been employed in the esterification reaction, it may be removed such as by distillation under reduced pressure. Any unremoved acid may then be neutralized such as with an alkaline solution.

The tolylethyl esters obtained by the processes herein described may be isolated and purified in any desired manner.

For example, the reaction mixture may, if desired, be repeatedly extracted with any suitable solvent, such as ether or benzene, to increase the yield and purity of the tolylethyl esters therein.

The extracts may then be combined and dried over a drying agent such as, for example, anhydrous sodium sulfate, after which the extraction solvent employed may be removed by distillation at atmospheric pressure. The residue may then be fractionally distilled in vacuo to obtain a purified tolylethyl ester of valeric acid.

Mixtures of alpha and beta tolylethyl derivatives, in any proportion, may be employed in the preparation of mixtures of alpha and beta tolylethyl esters of valeric acids.

Such mixtures of the alpha and beta forms of para tolylethyl esters of valeric acids may be desired in order to obtain a product possessing a desired boiling range, or desired volatility characteristics, or other desired properties.

For example, a mixture containing the desired proportion of each of the isomeric forms of tolylethyl halides may be reacted with a salt of valeric acid to obtain a tolylethyl ester fraction containing the desired proportion of the isomeric forms of tolylethyl esters of the acid. Mixtures containing the desired proportion of alpha and beta tolylethyl halides suitable for use in my process may be obtained, for example, by adding a hydrogen halide to methyl styrene under the proper conditions to give the desired mixture of isomeric tolylethyl halides, as set forth more fully in the second of my co-pending applications above referred to.

Similarly, a mixture of the isomeric forms of other tolylethyl derivatives, such as for example the tolylethyl alcohols, in the desired proportions, may be esterified to obtain a tolylethyl ester fraction containing the desired proportion of the isomeric forms of tolylethyl esters of valeric acid. Also a mixture of valeric acids or anhydrides, or derivatives thereof, may be employed in the foregoing processes.

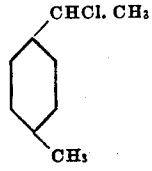
When mixtures of isomeric forms of tolylethyl esters of valeric acid are obtained, they may if desired be separated into fractions containing the individual isomers by any suitable method, such as for instance by fractionation.

As illustrative of the methods for preparing

various tolylethyl esters of valeric acids, the following examples are given:

Example I

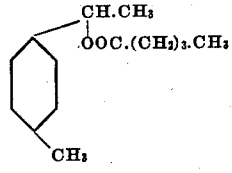
A 108 gram (0.7 mole) portion of alpha, para-tolylethyl chloride:



was added with stirring to a mixture of 127 grams (0.91 mole) of freshly prepared potassium n-valerate in 100 grams of n-valeric acid, the addition being carried out in a 1-liter flask fitted with a reflux condenser. The mixture was heated to 140° C. by means of an oil-bath and maintained at this temperature with good stirring for a period of five hours. It was allowed to cool and then treated with 10% sodium bicarbonate solution to neutralize the unchanged valeric acid present. The neutral mixture was then extracted with ether and dried over anhydrous sodium sulphate.

After the ether had been removed by heating on a hot water bath, the ester was distilled in vacuo, giving 110 grams of alpha, para-tolylethyl n-valerate.

This compound had the following structural formula and physical properties:



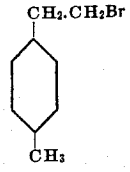
Boiling range=126–127° at 6 mm. Hg absolute
Density (d 20/4) =0.9697
Refractive index (n 20/d) =1.48805

The yield was 71.4% of theoretical.

The compound was a colorless, somewhat viscous liquid with a very pleasant odor.

Example II

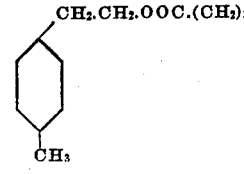
A solution of potassium n-valerate in n-valeric acid was made by stirring 210 grams (1.5 mols) of the fused salt into 250 grams of the anhydrous acid heated to 100° C. When a clear syrupy solution was obtained, 199 grams (1 mol) of beta, para-tolylethyl bromide:



was added slowly through the reflux condenser and the temperature was raised gradually to 170°. This temperature was maintained for a period of 13 hours, during which time a fine precipitate of potassium bromide separated from the reaction mixture.

The mixture was cooled and filtered by suction to remove the potassium bromide and excess potassium valerate, and the clear filtrate was distilled under reduced pressure to remove the major portion of the valeric acid which came over at a temperature of 50–60° at 4 mm. pressure absolute. The potassium bromide and excess potassium valerate were dissolved in cold water and extracted twice with ether to recover the small amount of absorbed ester. This extract was combined with the crude ester and treated with 10% sodium bicarbonate solution to neutralize the residual acid. It was then extracted with ether, dried with anhydrous sodium sulphate, and distilled.

Distillation under reduced pressure gave 172 grams of beta, para-tolylethyl n-valerate:



This compound had the following physical properties:

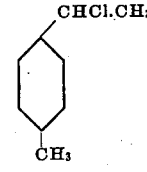
Boiling range=113–116° at 4 mm. Hg absolute
Density (d 20/4) =0.9720
Refractive index (n 20/d) =1.48855

This represented a yield conversion of 78.2%, based on the amount of beta, para-tolylethyl bromide used in the esterification.

The ester was obtained as a colorless, somewhat viscous liquid with an agreeable odor.

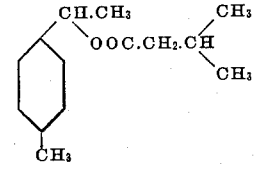
Example III

A solution of potassium isovalerate in isovaleric acid was made by stirring 210 grams (1.5 mols) of freshly fused potassium isovalerate into 300 grams of the anhydrous acid at a temperature of 90° C. When a clear syrupy solution was obtained, 155 grams (1 mol) of alpha, para-tolylethyl chloride:



was added slowly through the reflux condenser, and the temperature was raised gradually to 140° C. The temperature was kept at 140–145° for five hours with vigorous stirring, during which time a fine precipitate of potassium chloride separated out as a by-product of the reaction. The mixture was cooled and filtered by suction to remove the potassium chloride and excess potassium isovalerate, and the clear filtrate was distilled under reduced pressure to remove most of the isovaleric acid. The higher boiling liquid containing the ester was treated in the cold with 10% sodium bicarbonate solution to neutralize the residual acid. It was then extracted with ether, dried and distilled.

Distillation under reduced pressure gave 166 grams of alpha, para-tolylethyl isovalerate:



This compound had the following physical properties:

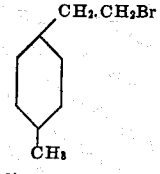
Boiling range—127–132° at 7 mm. Hg absolute
Density (d 20/4) =0.9642
Refractive index (n 20/d) =1.48532

The yield was 75.5% based on the weight of alpha, para-tolylethyl chloride used.

This product was a colorless, somewhat viscous liquid with an agreeable ester odor.

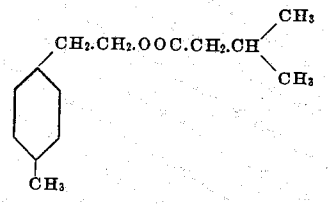
Example IV

A 210 gram portion (1.5 mols) of potassium isovalerate was added with stirring to 250 grams of isovaleric acid and heated to 100° C. until all the salt was dissolved. To this clear, syrupy solution was added dropwise, with continued stirring, 200 grams (1 mol) of beta, para-tolylethyl bromide:



in 50 minutes after which the temperature was raised to 165°. The temperature was kept at 163–167°, producing mild refluxing of the acid, for a period of 14 hours. The reaction mixture was then cooled and filtered to remove the potassium bromide and excess potassium isovalerate, and this solid matter was dissolved in water and extracted with ether to recover any absorbed ester. The clear filtrate was distilled to remove most of the isovaleric acid which came over at 49–51° at 3 mm. Hg absolute. The crude ester, combined with the ether extract, was treated with 10% sodium bicarbonate solution to neutralize the residual acid. It was then extracted with ether, dried with anhydrous sodium sulphate and distilled.

Distillation under reduced pressure gave 156 grams of beta, para-tolylethyl isovalerate:



This compound had the following physical properties:

Boiling range=99–104.5° at 1 mm. Hg absolute
Density (d 20/4) =0.9645
Refractive index (n 20/d) =1.48527

This weight of product represented a yield of 73.4%, based on the weight of beta, para-tolylethyl bromide used in the esterification.

The ester was obtained as a colorless, somewhat viscous liquid with a very sweet odor.

It will be understood of course, that tolylethyl esters of valeric acids may be prepared from pure methyl styrene or hydrocarbon fractions such as light oil fractions containing methyl styrene by processes which may be conducted on a continual, continuous, semi-continuous, or batch basis. For example, such a process may comprise first converting the methyl styrene into a tolylethyl derivative containing a substituent capable of being replaced with an ester group corresponding to the desired valeric acid, and thereafter effecting esterification of said derivative.

In this manner, the processes of the present invention may be combined with the processes disclosed and claimed in the second and/or third of my above referred to copending applications.

For example, in a preferred embodiment of this invention a tolylethyl halide may be prepared from a light oil methyl styrene fraction obtained by the distillation of light oil from oil gas and containing meta, para and ortho methyl styrenes and these tolylethyl halides may then be esterified to form the desired tolylethyl esters of valeric acid.

Likewise, a mixture of tolylethyl alcohols may be prepared from such a methyl styrene fraction, after which the tolyethyl alcohols may be converted into tolylethyl esters of valeric acid by esterification.

The esters of alkyl phenylethyl alcohols are, in general, practically colorless fluids possessing very pleasant odors.

As pointed out previously, esters of alkyl phenylethyl alcohols of the type more particularly described herein are well adapted for use as addition agents for soap and similar detergent materials. Esters of phenylethyl alcohols, when added to soap or similar products such as synthetic detergents and the like, serve not only to impart desirable odors thereto, but also assist in sealing the pores of such materials to prevent efflorescence and deterioration.

A preferred embodiment of this invention is the use of esters of the type described in conjunction with alkyl phenylethyl alcohols, and particularly tolylethyl alcohols. The use of the latter compounds as odorants and sealing agents for soaps and detergents is described and claimed in my copending application, Serial No. 434,789, filed March 14, 1942.

The addition of one or more esters of alkyl phenylethyl alcohols of the type described to bar soap as an odorant has been found to be particularly advantageous because of the unusually stable nature of these materials. A large number of perfuming agents now being used for this purpose suffer from a lack of stability, and when added to soap often result in the development of an undesirable odor after any extended period of storage thereof. This is primarily due to oxidation or hydrolysis of the odorant and its conversion into materials having undesirable or unpleasant odors.

Thus, for example, the exposure to light and air of soaps containing such odorants as phenyl acetaldehyde, benzaldehyde, anisic aldehyde, citral, lemon oil, citronellal, hydroxy citronellal, vanillin, and heliotropin, results in the development of disagreeable and unpleasant odors by oxidation, or by the action of other constituents in the soap, such as water.

Furthermore, certain of these odorants, such as, for example, vanillin and others having phenolic constituents, develop a dark color upon exposure to light and air, which generally is undesirable in soap and soap products.

Esters of alkyl phenylethyl alcohols, and particularly esters of tolylethyl alcohols of the type more specifically described herein, possess none of these undesirable properties. They are completely stable and resist the action of light and air for relatively long periods of time. They impart pleasant flowery or fruity odors to soap and similar products, the exact odor imparted to the soap being dependent upon the exact composition of the alkyl phenylethyl alcohol ester, or mixture of esters, employed. They have, therefore, been found to be highly desirable as odorants for such materials.

In this connection, it is well to point out that variations in odors of esters of the type described herein may be obtained by (1) a change in the

composition of the alcohol or alkyl phenylethyl derivative employed in the preparation of the ester, which may involve (*a*) a change in the alkyl groups substituted on the benzene nucleus, such as by replacing dimethyl phenylethyl alcohol with a tolylethyl alcohol, (*b*) a change in the position of such substituents, such as the use of meta tolylethyl alcohol in place of para tolyl ethyl alcohol, (*c*) a change in the position of the substituent, such as by the use of an alpha tolylethyl alcohol in place of a beta tolylethyl alcohol, and (*d*) the use of mixtures containing more than one alcohol, such as the use of mixtures of tolylethyl alcohols containing the meta, para, and ortho isomers; and (2) by a change in the composition of the acid, or acid derivative, or mixture of acids employed in the preparation of the ester, or mixture of esters. By a suitable choice of one or more of the foregoing variables, esters of alkyl phenylethyl alcohols possessing almost any desired odor may be prepared at will.

The reduction in quality of bar soap in the industry due to efflorescence represents a very considerable economic loss. Bar soap which has lost water by efflorescence presents a very unsightly appearance, becoming chalk-white and opaque in the case of white soap. In colored soap, the effect is even more pronounced as the area of efflorescence is marked by an opaque, off-colored zone. The addition of esters of alkyl phenylethyl alcohols of the type described herein to a soap or a soap product serves to effectively seal the pores on the surface thereof and retards the loss of water by efflorescence.

The property of preventing efflorescence and deterioration, when combined with the very advantageous odorizing properties of these derivatives, make them highly suitable for use in the soap industry.

In addition, these esters possess (1) unusually good solubility characteristics, (2) low viscosities, and (3) relatively high boiling points or ranges. The latter property is of very considerable value from the standpoint of the use of these materials in soaps and detergents, resulting in the production of very stable compositions.

The alkyl phenylethyl alcohol esters of the type described may be incorporated in soap in any desired manner. The quantity used will depend upon a number of factors, but quantities in the range of 0.05% to 5% by weight may be regarded as typical. The ester or esters may be used as such, or in suitable mixtures thereof, or in combination with other perfumes or additive agents.

Thus, for example, a mixture of 98 parts by weight of dried weighed soap chips and 2 parts by weight of a tolylethyl alcohol ester of the type described may be thoroughly mixed and fed into a milling machine. The milled soap then may be plodded, stamped, and molded, or otherwise processed. The bar soap thus obtained will be found to possess a very agreeable odor and to be unusually resistant to efflorescence.

In addition to their use in bar soap, alkyl phenylethyl alcohol esters of the type described herein also may be employed to advantage in other types of soap, such as, for example, flake, chip, powder, or bead forms. In addition, they may be incorporated in synthetic detergents, such as sodium lauryl sulfonate and alkyl benzene sulfonate sodium salt.

The soaps and synthetic detergents to which this invention relates may be conveniently classified under the generic term "detergents," illustrative formula for which are as follows:

RCOOM in which R stands for alkyl and M stands for an alkali metal such as sodium and potassium. Examples are alkali metal salts of fatty acids, such as soaps.

$(MSO_3)_x RCOOM$ in which R stands for

$$C_nH_{2n}+1$$

M stands for an alkali metal such as sodium or potassium, and x stands for any integer. Examples are alkali metal salts of sulfonated fatty acids.

$(SO_3M)_x ROH$ in which R stands for $C_nH_{2n}+1$, M stands for an alkali metal such as sodium or potassium, and x stands for any integer. Examples are sodium lauryl sulfonate.

$(SO_3M)_x R_1R_2$ in which M stands for an alkali metal such as sodium or potassium, x is an integer, R_1 stands for an aryl or substituted aryl group, and R_2 stands for an alkyl or substituted alkyl group. Examples are alkali metal salts of sulfonated alkylated aromatic compounds.

Generically speaking, detergent compounds contain more than 15 carbon atoms. Thus, soaps used as detergents are generally speaking alkali metal salts of fatty acids containing more than 15 carbon atoms, examples of which are the sodium and potassium salts of palmitic, oleic, and stearic acids.

While compounds and products of a particular nature have been specifically described, it is to be understood that these are by way of illustration. Therefore, changes, omissions, additions, substitutions and/or modifications might be made within the scope of the claims without departing from the spirit of the invention, which is intended to be limited only as required by the prior art.

I claim:

1. A detergent composition, comprising a mixture of an ester of tolyl ethyl alcohol and an alkali metal soap, said ester of tolyl ethyl alcohol being present in said mixture in a proportion between 0.05 and 5% by weight of said soap.

2. A detergent composition, comprising alkali metal soap in admixture with from 0.05 to 5% by weight of a mixture of esters of tolyl ethyl alcohol, said mixture of esters comprising from 50 to 75% of an ester of meta tolyl ethyl alcohol, from 20 to 50% of an ester of para tolyl ethyl alcohol, and from 1 to 10% of an ester of ortho tolyl ethyl alcohol.

3. A detergent composition, comprising an alkali metal soap in admixture with from 0.05 to 5% by weight of a mixture of esters of tolyl ethyl alcohol, said mixture of esters containing from 60 to 70% of an ester of meta tolyl ethyl alcohol, from 25 to 40% of an ester of para tolyl ester alcohol, and from 2 to 8% of an ester of ortho tolyl ethyl alcohol.

4. A detergent composition, comprising a mixture of an alkali metal soap with from 0.05 to 5% by weight of a fatty acid ester of tolyl ethyl alcohol in which an ester of alpha tolyl ethyl alcohol preponderates.

5. A detergent composition, comprising an alkali metal soap having admixed therewith from 0.05 to 5% by weight of a fatty acid ester of tolyl ethyl alcohol which is preponderantly in the form of an ester of beta tolyl ethyl alcohol.

6. A detergent composition comprising alkali metal soap in admixture with from 0.05 to 5% by weight of tolyl ethyl valerate.

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