

## UNITED STATES PATENT OFFICE

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## DETERGENTS

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The present invention relates to detergents and wetting agents, particularly to materials of this type which are tasteless and therefore especially useful in the formulation of dentifrices, mouth washes and the like. Specifically the invention relates to new compounds that possess general properties making them especially suitable for use as detergents, wetting agents, emulsifying agents and the like and which are characterized by a substantial absence of odor and taste. These compounds are higher alkyl esters of sulfonated monocarboxylic aromatic acids and salts thereof.

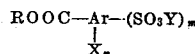
The detergents heretofore known comprised such varied substances as ordinary fatty soaps and sulfated and sulfonated compounds of varying degrees of complexity. Of these materials, sulfonated alkylated aromatic sulfonic acids such as alkylbenzene sulfonic acids and alkylphenol sulfonic acids and their salts are especially useful materials since they are characterized by especially high surface activity or capillary activity characteristics and are of low cost. However, soap and alkylated aromatic sulfonic acids, even in the purest form in which it has been possible to prepare them generally have perceptible tastes and odors which militate against their extensive use in preparations destined for oral administration. The alkyl groups or radicals of alkylated aromatic sulfonic acids are generally derived from petroleum hydrocarbon fractions, either by effecting the alkylation of the aromatic hydrocarbon or phenol with a chlorinated petroleum fraction or with a dehydrogenated petroleum fraction (olefin fraction), for example, according to the methods disclosed in Kyrides Patents Nos. 2,161,173 and 2,161,174 and Flett Patents Nos. 2,134,711 and 2,134,712. Much of the taste and odor of the resulting alkylated aromatic sulfonic acids is attributable to the impurities present in the petroleum fractions, particularly to sulfur and nitrogen compounds therein, which are not readily removed by distillation. Some degree of improvement in taste and odor of alkylated aromatic sulfonic acids can be realized by subjecting the petroleum hydrocarbon fractions to chemical treatments but such refining procedures are costly. However, even by means of such alternatives it is not possible to remove the inherent taste and odor of alkylated aromatic sulfonic acids. Detergent compounds having no substantial odor and taste are desirable, especially for the preparation of materials which are intended for oral administration, for example, dentifrices, mouth washes and the like.

It is the principal object of the present inven-

tion to provide a detergent of greatly improved odor and taste characteristics. A further object of the invention is to provide methods of preparing such improved detergents. In the description which follows hereinafter, other objects and advantages of the invention, some of which are not specifically referred to, will be apparent to those skilled in the art.

This invention is based upon the discovery that higher alkyl esters of monocarboxylic aromatic sulfonic acids and their water-soluble salts are effective detergents which are similar to alkylated aromatic sulfonic acids in their surface activity and capillary activity characteristics and that these compounds are further characterized by a remarkable freedom from inherent odor and taste. The alkylated monocarboxylic aromatic sulfonic acids and their salts lend themselves much more readily to purification than alkylated aromatic sulfonic acids and when in the pure state have considerably more freedom from inherent odor and taste than the corresponding alkylated aromatic hydrocarbon and alkylated phenol sulfonic acids and their salts. By carefully controlling the esterification conditions (for example, by heating at temperatures not substantially in excess of 135° C. in esterifying meta-sulfobenzonic acid with a commercial mixture of higher alcohols) pure products requiring no further crystallization can be obtained.

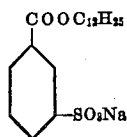
The compounds contemplated by the present invention are alkyl esters of monocarboxylic aromatic sulfonic acids and salts thereof having the general formula



in which Ar is an aryl nucleus derived from hydrocarbons such as benzene, naphthalene, diphenyl and the like; X is a substituent such as a hydrogen, hydroxyl, halogen or a similar radical; Y is hydrogen or an alkali-metal, calcium or magnesium radical;  $n$  and  $m$  are whole numbers which may be one or a greater number, indicating that the compounds are mono or polysulfonated or mono or polyhalogenated or hydroxylated; and R is an alkyl radical having from 8 to 18 carbon atoms. The group X may be substituted in any of the various positions of the aromatic nucleus; thus, in the case of benzene, it may be ortho, meta, or para to the carboxyl group. The compounds contain a single alkyl substituent and that appears in the carboxyl group of the aromatic sulfonic acid.

Typical preferred compounds of the invention are alkyl esters of ortho, meta, and para-sulfobenzoic acids and alkyl esters of sulfosalicylic acid and salts thereof. The alkyl radicals thereof may be octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl or octadecyl radicals, either straight or branched-chain, although straight-chain alkyl radicals are preferred. Thus, for example, the alkyl radical may be normal-octyl, 2-ethylhexyl, normal-dodecyl and the like. The preferred alkyl radicals are those containing 10 to 16 carbon atoms. Mixtures of compounds having alkyl radicals containing from 10 to 16 carbon atoms are also contemplated by the present invention.

Specific preferred compounds are shown in the examples which follow hereinafter. The compounds correspond to the generic formula hereinabove and the method of naming them is exemplified by reference to the specific compound denominated, dodecyl-m-sodium sulfobenzoate, which has the formula:



The naming of the other compounds follows this system of nomenclature, the alkyl substituent being understood to be on the carboxyl group and the salt-forming metal being understood to be on the sulfonic acid radical, whereas the positions o, m, and p refer to the relative positions of the carboxyl and sulfonic acid radicals with respect to each other in the benzene nucleus where these positions are known and indicated. The term "Loralkyl" is used to refer to alkyl radicals containing from 10 to 16 carbon atoms which result from esterification of the sulfoaromatic acid with commercial alcohol mixtures such as "Lorol."

The compounds of the invention are preferably prepared by reacting an alcohol with the sulfonated aromatic acid or its anhydride or acid chloride. Thus a dodecyl ester of ortho-sulfobenzoic acid may be prepared by reacting dodecyl alcohol (which may be derived from cocoanut oil) with ortho-sulfobenzoic acid anhydride. Other known methods of synthesis may be used, however. Thus, for example, benzoic acid may be esterified with dodecyl alcohol and the resulting dodecyl benzoate may thereafter be sulfonated. This latter procedure, when not carefully controlled, leads to the production of by-products which render the purification of the resulting dodecyl ester of sulfobenzoic acid difficult. The simple alkyl esters of monocarboxylic aromatic sulfonic acids, if contaminated with by-products, can be further purified by crystallization from aqueous solution and when thus purified are substantially odorless and tasteless products having pronounced foaming, wetting and detergent properties. By controlling carefully the esterification reaction, products requiring no further extensive purification treatment may be obtained, however.

There is no substantial difference in detergency between corresponding alkyl esters of isomeric sulfoaromatic acids. The dodecyl esters of ortho, meta, and para-sulfobenzoic acids, for example, have approximately the same effectiveness although the ortho appears to be most efficient while the para isomer, which is the least soluble in water, is not quite as efficient in hard water

as the others. Since meta-sulfobenzoic acid is the isomer obtained in preponderance when benzoic acid is sulfonated, the present invention is directed particularly to the alkyl esters of this acid.

In the examples which follow, typical compounds of the invention and methods for their preparation are described.

#### Example 1.—Octyl-o-sodium sulfobenzoate

Into a flask attached to a Stark and Dean moisture trap and a condenser are placed 15 grams of ortho-sulfobenzoic anhydride, 15 grams of 2-ethylhexanol and 50 cc. of benzene. The benzene is added to aid in carrying over any water which is originally present and that formed in the reaction. Toluene or xylenes may be used in place of benzene for this purpose. The charge in the flask is then heated for approximately 2 hours so that a slow reflux of the benzene occurs. The period of heating may be varied somewhat but is generally conducted until water stops collecting in the moisture trap. Approximately 400 cc. of water is added to the cooled mixture after the esterification reaction is completed and the resulting emulsion is allowed to break. The water layer is thereafter separated and neutralized by the addition of an aqueous solution of sodium hydroxide and the resulting slurry is dried, preferably by means of a drum-drier.

In using greater quantities of reactants it is desirable prior to neutralization to remove the benzene or other liquid used for carrying over the water.

The resulting octyl-o-sodium sulfobenzoate may be purified if desired by crystallization from water or other solvent.

#### Example 2.—Octyl-o-sulfobenzoate and salts thereof

To obtain octyl-o-sulfobenzoate, the neutralization with sodium hydroxide in the foregoing example may be omitted or the sodium salt therein prepared may be acidified with a strong mineral acid and the resulting product, octyl-o-sulfobenzoate, may be recovered in conventional manner. Salts of other metals may be made by substituting the sodium hydroxide in the foregoing with a hydroxide or in some cases a carbonate of the desired metal.

#### Example 3.—Dodecyl-o-sodium sulfobenzoate

A mixture of 15 g. of o-sulfobenzoic anhydride, 15 g. of a 105–110°/1 mm. fraction of the commercial mixture of higher alcohols known as Lorol, 7 drops of 100% phosphoric acid and 50 cc. of benzene is heated as in Example 1 for 3 hours. The reaction mixture is cooled, 500 cc. of water are added and it is neutralized as before. After standing, the oily layer is separated and discarded and the water layer is drum-dried to give a light cream-colored product.

#### Example 4.—Dedecyl-o-sodium sulfobenzoate crystallized

Instead of drum-drying the water layer in Example 3, it may be concentrated somewhat and allowed to crystallize. The resulting crystals of dodecyl-o-sodium sulfobenzoate, which are colorless, may be filtered off and dried in the air.

#### Example 5.—Tetradecyl-o-sodium sulfobenzoate

A mixture of 15.2 g. of o-sulfobenzoic anhydride 30 g. of a 115–120°/0.2 mm. (tetradecyl al-

cohol) fraction of the commercial mixture of higher alcohols known as Lorol, 0.5 g. of 100% phosphoric acid and 100 g. of benzene is heated as in Example 1 by direct flame so that the benzene refluxed slowly for about 2.5 hours. The reaction product is cooled and 600 cc. of water are added and the mixture is neutralized as before. The resulting emulsion breaks with difficulty. The entire product may be drum-dried without separation. The dry product may be extracted with hexane, dissolved in water and again drum-dried.

#### Example 6—Loralkyl o-sodium sulfobenzoate

A mixture of 18.4 g. of o-sulfobenzoic anhydride, 18.6 g. of commercial Lorol, 0.5 g. of 100% phosphoric acid and 25 cc. of benzene is refluxed slowly for 7 hours over a flame as in Example 1. The mixture is cooled and 400 cc. of water are added. The product is neutralized with caustic soda as before. The resulting suspension is then drum-dried. The product is light cream-colored.

#### Example 7—Dodecyl-o-sodium sulfobenzoate

A mixture of 18 g. of o-sulfobenzoic anhydride, 17 g. of a dodecyl alcohol fraction (105–110°/1 mm.) of Lorol and 50 cc. of benzene is heated under reflux for 5 hours. The product is recovered as in Example 6.

#### Example 8—Dodecyl-m-sodium sulfobenzoate

By substituting m-sulfobenzoic acid for o-sulfobenzoic anhydride in Example 7 and recovering the product as therein indicated, dodecyl-m-sodium sulfobenzoate in the form of a slightly yellow, fluffy powder is obtained.

#### Example 9—Dodecyl-p-sodium sulfobenzoate

By substituting p-sulfobenzoic acid for o-sulfobenzoic anhydride in Example 7 and recovering the product as therein indicated, dodecyl-p-sodium sulfobenzoate is obtained.

#### Example 10—Octyl sodium sulfosalicylate

A mixture of 63.5 g. of sulfosalicylic acid, 78 g. of octyl alcohol (2-ethyl hexanol) and 100 cc. of toluene is refluxed as in Example 1 until 20.5 cc. of water were taken off. The product is neutralized with sodium hydroxide solution, diluted to 800 cc. and drum-dried. The product may be taken up in water and again drum-dried if desired.

#### Example 11—Dodecyl sodium sulfosalicylate

A mixture of 115 g. of dodecyl alcohol, 63.5 g. of sulfosalicylic acid and 90 cc. of toluene is heated as in Example 1. In 3.5 hours, 18.5 cc. of water are taken off. The product is neutralized in water with sodium hydroxide, made up to 1 liter, about 20 cc. of alcohol is added, and the mass is filtered and then drum-dried.

#### Example 12—Loralkyl sodium sulfosalicylate

A mixture of 100 g. of sulfosalicylic acid, 100 g. of the commercial mixture of alcohols known as Lorol, 0.5 g. of 100% phosphoric acid ( $H_3PO_4$ ) and 220 cc. of benzene is heated in an oil bath. In 55 hours approximately 22 cc. of water are taken off. The product is recovered as in Example 1.

#### Example 13—Loralkyl m-sodium sulfobenzoate

A mixture of 25 g. of m-sulfobenzoic acid, 23 g. of Lorol, 0.5 g. of 100% phosphoric acid and 50 cc. of benzene in an apparatus such as described in Example 1 is heated in an oil bath at a temperature below or at 135° C. until about 5 cc. of water are taken off. The product is then neutralized with caustic soda, made up to 800 cc. and drum-dried at 80#/sq. in. steam pressure as before.

**Wetting out tests.**—The compounds as above prepared were subjected to Draves' regulation wetting out tests at 25° C. These tests were made on aqueous solutions of the compounds and were compared with tests made under identical conditions with comparable wetting agents. The numbers preceding the name of the compound in the table refer to the example hereinabove in which its preparation is described. The solutions were tested by placing a cotton skein in each and determining the period required for the skein to become completely wetted by the solution. The periods in seconds required for wetting at the various dilutions are as indicated in the table:

| Compound                                       | Dilution (percent solution) |       |       |       |       |       |
|------------------------------------------------|-----------------------------|-------|-------|-------|-------|-------|
|                                                | 0.5                         | 0.25  | 0.125 | 0.062 | 0.032 | 0.016 |
| 1. Octyl-o-sodium sulfobenzoate                | 17.4                        | 180+  | —     | —     | —     | —     |
| 3. Dodecyl-o-sodium sulfobenzoate              | 3.2                         | 5.6   | 7.3   | 15.8  | 44.1  | 180+  |
| 4. Dodecyl-o-sodium sulfobenzoate crystallized | —                           | 4.7   | 7.5   | 15.0  | 41.4  | 180+  |
| 5. Tetradecyl-o-sodium sulfobenzoate           | —                           | 15.8  | 21.1  | 48    | 99    | 180+  |
| 6. Loralkyl o-sodium sulfobenzoate             | 11.0                        | 20.1  | 26.3  | 41.2  | 102.4 | 180+  |
| 7. Dodecyl-o-sodium sulfobenzoate              | 4.1                         | 5.6   | 9.6   | 20.1  | 41.6  | 180+  |
| 8. Dodecyl-m-sodium sulfobenzoate              | 11.4                        | 19.1  | 24    | 45.8  | 121   | 180+  |
| 9. Dodecyl-p-sodium sulfobenzoate              | 43                          | 73    | 180+  | —     | —     | —     |
| 10. Octyl-sodium sulfosalicylate               | 9.8                         | 107.3 | 180+  | —     | —     | —     |
| 11. Dodecyl sodium sulfosalicylate             | 5.3                         | 9.2   | 20.4  | 45.3  | 151.1 | 180+  |
| 12. Loralkyl sodium sulfosalicylate            | 29.2                        | 42.2  | 56.9  | 121.9 | 180+  | —     |
| 13. Loralkyl m-sodium sulfobenzoate            | 24.1                        | 36.6  | 51.5  | 88.6  | 180+  | —     |
| Santomer 3                                     | 2.8                         | 3.9   | 7.9   | 19.6  | 99.0+ | —     |
| Dodecyl sodium sulfophenylacetate              | 43.9                        | 85.8  | 180+  | —     | —     | —     |

**Standard soil launderometer tests.**—The compounds prepared in the examples hereinabove were subjected to standard soil launderometer tests in comparison with known detergents. This standard soil washing test is conducted as follows: To a cotton fabric is applied under controlled conditions a standard soil solution composed of a suspension of carbon black, vegetable oils and mineral oils in water. The fabric is then aged for a predetermined period. The aging of the fabric is important because the soil is more difficult to remove as it becomes older. The soiled fabric is then washed in a launderometer and each sample is tested in triplicate at various wash intervals (10, 20, 30 and 40 minutes in these tests). The washed sample is then dried and the lightening of the fabric is determined using a Pulfrich photometer or similar instrument. The relative detergency is thus established.

In the table are indicated the various percentages of soil removed by washing with 0.2% solutions of the compounds dissolved in both hard and in soft water. The values for the different compounds vary with the different series

of tests, as can be observed by the different results for the comparative commercial product, Gardinol-WA, in the various series. In using these values, therefore, accurate comparison can be made only within the same series and not throughout the table.

*Soft water (50 P. P. M.)*

| Compound                                 | Lather (Inches) | 10 min. | 20 min. | 30 min. | 40 min. |
|------------------------------------------|-----------------|---------|---------|---------|---------|
| <i>Series I</i>                          |                 |         |         |         |         |
| Gardinol-WA.....                         | 4               | 29      | 43      | 52      | 58      |
| 3. Dodecyl-o-sodium sulfobenzoate.....   | 4               | 35      | 44      | 47      | 50      |
| 10. Octyl sodium sulfosalicylate.....    | 0               | 15      | 16      | 17      | 19      |
| <i>Series II</i>                         |                 |         |         |         |         |
| Gardinol-WA.....                         | 4               | 30      | 44      | 53      | 63      |
| Loralkyl-o-sodium sulfobenzoate.....     | 4               | 30      | 46      | 49      | 56      |
| <i>Series III</i>                        |                 |         |         |         |         |
| Gardinol-WA.....                         | 4               | 31      | 40      | 50      | 57      |
| Dodecyl sodium sulfophenylacetate.....   | ½               | 21      | 31      | 35      | 39      |
| 11. Dodecyl sodium sulfosalicylate.....  | 4               | 27      | 37      | 44      | 47      |
| <i>Series IV</i>                         |                 |         |         |         |         |
| Gardinol-WA.....                         | 4               | 21      | 33      | 40      | 43      |
| 7. Dodecyl-o-sodium sulfobenzoate.....   | 3               | 21      | 31      | 36      | 40      |
| 8. Dodecyl-m-sodium sulfobenzoate.....   | 4               | 23      | 31      | 38      | 41      |
| 9. Dodecyl-p-sodium sulfobenzoate.....   | 4               | 24      | 36      | 42      | 45      |
| 13. Loralkyl-m-sodium sulfobenzoate..... | 4               | 30      | 39      | 45      | 46      |
| <i>Series V</i>                          |                 |         |         |         |         |
| Gardinol-WA.....                         |                 | 27      | 40      | 50      | 56      |
| 12. Loralkyl sodium sulfosalicylate..... |                 | 32      | 44      | 52      | 55      |

*Hard water (300 P. P. M.)*

| Compound                                  | Lather (Inches) | 10 min. | 20 min. | 30 min. | 40 min. |
|-------------------------------------------|-----------------|---------|---------|---------|---------|
| <i>Series I</i>                           |                 |         |         |         |         |
| Gardinol-WA.....                          | 4               | 32      | 44      | 53      | 58      |
| 3. Dodecyl-o-sodium sulfobenzoate.....    | 4               | 38      | 44      | 50      | 55      |
| 10. Octyl sodium sulfosalicylate.....     | 0               | 15      | 12      | 13      | 13      |
| <i>Series II</i>                          |                 |         |         |         |         |
| Gardinol-WA.....                          | 4               | 40      | 49      | 52      | 57      |
| 5. Tetradecyl-o-sodium sulfobenzoate..... | 4               | 34      | 43      | 52      | 56      |
| 6. Loralkyl-o-sodium sulfobenzoate.....   | 4               | 39      | 48      | 54      | 58      |
| <i>Series III</i>                         |                 |         |         |         |         |
| Gardinol-WA.....                          | 4               | 32      | 40      | 49      | 51      |
| Dodecyl sodium sulfophenylacetate.....    | ½               | 23      | 34      | 44      | 47      |
| 11. Dodecyl sodium sulfosalicylate.....   | 4               | 36      | 51      | 55      | 58      |
| <i>Series IV</i>                          |                 |         |         |         |         |
| Gardinol-WA.....                          | 4               | 25      | 34      | 41      | 46      |
| 7. Dodecyl-o-sodium sulfobenzoate.....    | 4               | 27      | 36      | 43      | 46      |
| 8. Dodecyl-m-sodium sulfobenzoate.....    | 4               | 28      | 37      | 44      | 50      |
| 9. Dodecyl-p-sodium sulfobenzoate.....    | ½               | 14      | 20      | 24      | 27      |
| 13. Loralkyl m-sodium sulfobenzoate.....  | 4               | 36      | 42      | 47      | 51      |
| <i>Series V</i>                           |                 |         |         |         |         |
| Gardinol-WA.....                          |                 | 28      | 38      | 44      | 48      |
| 12. Loralkyl sodium sulfosalicylate.....  |                 | 28      | 40      | 44      | 50      |

The compounds of this invention in general exhibit high water solubility and great surface activity. They are useful for general purposes

of wetting agents, detergents, foaming and emulsifying agents and are of advantage for use in dyeing processes, textile treating processes, in ore flotation, for breaking petroleum emulsions, in plaster, cement and ceramic mixes, as dispersing agents for germicides and insecticides, in printing inks, and for similar uses. Of course, no single compound shows all these properties to a marked degree. A good wetting agent is not necessarily the best detergent or best textile softening agent but it is an advantage of this group of compounds that by a selection of the proper alkyl chain length and configuration for the alkyl chain, an agent possessing a particular surface active property to a marked degree can be obtained.

The compounds described herein when used as detergents may be used in pure form or in admixture with each other or with detergent builders such as sodium sulfate, magnesium sulfate, sodium carbonate and the like.

The compounds of the present invention are particularly useful for the production of powder, liquid, cream or paste dentifrices. Because of their substantial freedom from taste and odor they may be used advantageously for complete or partial substitution of conventional deterging, cleansing, lathering or emulsifying ingredients of such compositions, for example, in complete or partial substitution for soap, sulfonated oils such as sulfonated castor oil, saponins, sulfated higher alcohols such as commercial products known as "Gardinals," alkylated aromatic sulfonic acids such as isopropyl naphthalene sulfonic acid and the commercial products known under the trade names, Nacconol and Santomerase. Dentifrice compositions generally contain an abrasive or polishing base such as chalk or precipitated calcium carbonate, magnesium carbonate, magnesium oxide, dicalcium phosphate, tricalcium phosphate, calcium sulfate, talc, kaolin (or elutriated kaolins such as bolus alba), silica gel, aluminum silicate, or bentonite; together with a binding agent such as gum arabic, gum tragacanth, gum karaya, starch or dextrin; an excipient such as water, glycerol, or the like; and a flavoring material such as oil of peppermint, oil of cloves, oil of wintergreen, methyl salicylate, phenyl salicylate, lemon oil, saccharin or sugar; with or without flavoring materials having a disinfecting action such as thymol, menthol and eucalyptol; and may contain as additional ingredients alkali-metal salts or mucin solvents such as disodium phosphate, trisodium phosphate, alkali metal metaphosphates or pyrophosphates (tetrasodium pyrophosphate, for example), sodium carbonate, sodium bicarbonate, or borax.

Preferred dentifrice compositions for which the compounds of the present invention are particularly useful are those containing the ingredients in the proportions specified in the examples which follow:

*Example 15—Tooth paste*

| Parts by weight                     |       |
|-------------------------------------|-------|
| Glycerol.....                       | 23.56 |
| Water.....                          | 21.26 |
| Calcium chloride.....               | 0.87  |
| Calcium sulfate.....                | 89.5  |
| Gum tragacanth.....                 | 1.09  |
| Saccharin (aqueous solution).....   | 0.22  |
| Oil of peppermint.....              | 1.15  |
| Tetrasodium pyrophosphate.....      | 3.58  |
| Dodecyl-o-sodium sulfobenzoate..... | 4.47  |

*Example 16—Tooth paste*

|                                     | Parts by weight |
|-------------------------------------|-----------------|
| Glycerol.....                       | 74              |
| Water.....                          | 26              |
| Calcium sulfate.....                | 79              |
| Tricalcium phosphate.....           | 27              |
| Gum tragacanth.....                 | 2               |
| Saccharin (aqueous solution).....   | 0.2             |
| Oil of wintergreen.....             | 2               |
| Tetrasodium pyrophosphate.....      | 4.6             |
| Dodecyl sodium sulfosalicylate..... | 5               |

*Example 17—Tooth paste*

|                                     | Parts by weight |
|-------------------------------------|-----------------|
| Glycerol.....                       | 109             |
| Water.....                          | 25              |
| Calcium chloride.....               | 0.8             |
| Dicalcium phosphate.....            | 270             |
| Gum tragacanth.....                 | 2.4             |
| Gum karaya.....                     | 2.4             |
| Saccharin (aqueous solution).....   | 2.4             |
| Benzoic acid.....                   | 0.18            |
| Eucalyptol.....                     | 2.4             |
| Dodecyl m-sodium sulfobenzoate..... | 7.6             |

Inasmuch as the above description comprises preferred embodiments of the invention it is to be understood that the invention is not limited thereto and that changes and modifications may be made therein without departing substantially from the invention, which is defined in the appended claims.

**We claim:**

1. A sodium salt of a monoalkyl ester of a monocarboxylic aromatic sulfonic acid selected from the group consisting of sulfobenzoic acids and sulfosalicylic acids in which the alkyl group has not less than 8 and not more than 12 carbon atoms and is attached to the carboxyl group.
2. A sodium salt of a dodecyl ester of a sulfobenzoic acid in which the dodecyl group is attached to the carboxyl group.
3. A sodium salt of a dodecyl ester of a sulfosalicylic acid in which the dodecyl group is attached to the carboxyl group.
4. A water-soluble metal salt of a monoalkyl ester of a monocarboxylic aromatic sulfonic acid selected from the group consisting of sulfobenzoic acids and sulfosalicylic acids, in which the alkyl group has from 8 to 12 carbon atoms and is attached to the carboxyl group, said salt having a metal residue selected from the group consisting of alkali-metals, calcium and magnesium.
5. A monoalkyl ester of a monocarboxylic aromatic sulfonic acid selected from the group consisting of sulfobenzoic acids and sulfosalicylic acids, in which the alkyl group has from 8 to 12 carbon atoms and is attached to the carboxyl group.
6. A sodium salt of a dodecyl ester of a meta-sulfobenzoic acid, in which the dodecyl group is attached to the carboxyl group.

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