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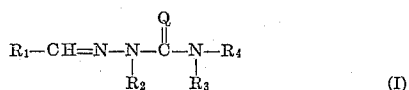
SALICYLALDEHYDE-SEMICARBAZONES

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No Drawing. Filed Apr. 26, 1962, Ser. No. 190,257
8 Claims. (Cl. 260-552)

This application is a continuation-in-part of application Serial No. 854,612, filed November 23, 1959, now abandoned.

This invention relates to new germicides and to detergent compositions containing said germicides. More specifically, this invention relates to compounds of the formula:



wherein R_1 is a halogenated ortho-hydroxyaryl radical of less than three 6-membered rings, the halogens of which have an atomic number between 16 and 36, R_2 is hydrogen or lower alkyl, R_3 is either hydrogen, lower alkyl, aralkyl (e.g., benzyl and phenethyl) cycloalkyl, aryl (e.g., phenyl, tolyl, or xylyl), R_4 is aryl (e.g., phenyl, tolyl, xylyl and naphthyl) and Q is oxo or thiono. More specifically, it relates further to detergent compositions comprising non-ionic or anionic detergents and germicides of the class represented by Formula I.

In recent years, increased attention has been given to the development of textile finishes which have become known as purifying finishes. These are intended to reduce the number of microorganisms able to exist on the material. These purifying finishes, when applied to articles of clothing worn close to the body, are also helpful in preventing the development of body odors.

A satisfactory purifying finish should be durable and active at low concentrations against a broad spectrum of microorganisms. It should be non-toxic and non-allergenic. Yet it must maintain its activity even against new strains of organisms which may develop as a result of using the germicidal agent in the finish. It should impart little or no color to the fabric and should be stable with respect to color and activity for many months under storage and shipping conditions. It should be resistant to the conditions used in laundering and dry cleaning. It should impart little or no modification of the hand of the textile and be substantive to the fiber. It should be compatible with dyes and resins found in textile finishes.

Various textile purifying finishes containing anti-bacterial substances such as hexachlorophene, tetrachlorophene, quaternary ammonium compounds such as dimethylbenzyl ammonium chloride, organo-metallic complexes of mercury, copper and silver, and others have been used, but these are for the most part non-durable and unsatisfactory in other respects, especially in their inability to exhaust from a laundry bath.

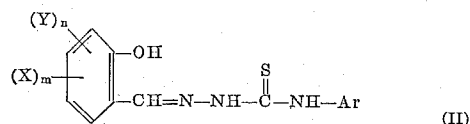
Substantivity on the fiber and durability of the anti-bacterial action are probably the two most important attributes for a purifying finish. Without substantivity, the germicide is merely a coating to be rubbed or washed off by the first treatment to which it is subjected. Sub-

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stantivity, or affinity for the fiber, is, therefore, one of the main factors in durability; however, durability must also be a function of the stability of the germicidal compound to oxidation by air and degradation by light and heat or the like.

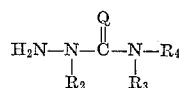
An especially important aspect of substantivity is the ability to exhaust from laundering baths in the same way that a dye exhausts from a dyebath. If a germicidal soap is to have the widest utility, it must be applicable from regular laundering solutions during the laundering operations, whether in the home, the hospital or the commercial laundry. Repeated launderings will then have the effect of increasing, rather than depleting the concentration of the germicide on the fiber. Known germicidal compositions lack true substantivity under these conditions and thus are drastically limited in their effective utility.

In accordance with this invention, it has been found that a new class of compounds are durably germicidal and at the same time are substantive to textiles under laundering conditions thus making them eminently suitable as textile purifying finishes. This class of compounds, defined above, has high anti-bacterial action and is fast to washing. Within this class is an especially preferred group of substantive germicides represented by the formula:

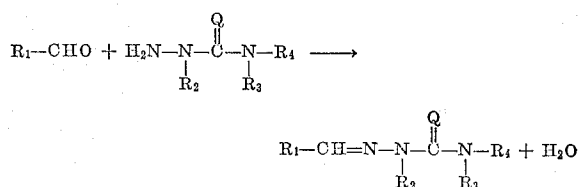


wherein X is a halogen of atomic number between 16 and 36, m is 1, 2 or 3, Y is lower alkyl or nitro, n is 0, 1 or 2 and Ar is an aromatic, carbocyclic aryl radical of less than three 6-membered rings which may be substituted by chlorine, bromine, lower alkoxy and lower alkyl radicals.

The new compounds of this invention may be prepared by condensing a halogenated ortho-hydroxyaryl aldehyde wherein the aryl moiety corresponds to " R_1 " defined above (especially halogenated salicylaldehydes) with a 4-aryl-3-semicarbazide or a 4-aryl-3-thio semicarbazide of the formula:



wherein R_2 , R_3 , R_4 and Q are as defined above. The condensation reaction is conducted under conventional reaction conditions and proceeds along the lines of the following equation:



Generally, any halogenated ortho-hydroxyaryl aldehyde consistent with the definition of R_1 may be used in the preparation of the germicides of this invention. Preferred aldehydes are halogenated salicylaldehydes represented by such compounds as 3,5-dichlorosalicylaldehyde, 5-chlorosalicylaldehyde, 5-nitro-3-chlorosalicylaldehyde, 5-methyl-3-bromosalicylaldehyde, 5-methyl-3-chlorosalicylaldehyde, 3-methyl-5-chlorosalicylaldehyde and 3-bromo-5-t-butylsalicylaldehyde.

Illustrative of the thiosemicarbazides and semicarbazides useful for the practice of this invention are: 4-phenyl-3-thiosemicarbazide, 4-o, m or p-tolyl-3-thiosemicarbazide, 4-o, m or p-methoxyphenyl-3-thiosemicarbazide, 4-o, m or p-chlorophenyl-3-thiosemicarbazide, 4-(3,5-dichlorophenyl)-3-thiosemicarbazide, 4-(3,4,5-trichlorophenyl)-3-thiosemicarbazide, 4-(o, m or p-bromophenyl)-3-thiosemicarbazide, 4-(3,5-dibromophenyl)-3-thiosemicarbazide, 4-(α - or β -naphthyl)-3-thiosemicarbazide, 4-(o-, m-, or p-biphenyl)-3-thiosemicarbazide, 4-phenyl-3-semicarbazide, 4-(o, m or p-chlorophenyl)-3-semicarbazide, 4-(o, m or p-tolyl)-3-semicarbazide and 4-(α - or β -naphthyl)-3-semicarbazide.

The preferred compounds of this invention are those in which R_1 is a halogenated ortho hydroxyphenyl group, the 4-aryl group (i.e., the R_4 radical) is a monocyclic radical and both R_2 and R_3 are hydrogen.

The compounds of this invention are effective against Gram positive bacteria including *Staphylococcus aureus* and other Gram positive bacteria including those known to decompose perspiration into odoriferous products. When applied to cloth from a solution (by a padding procedure), they suppress *Staphylococcus aureus* development in the contact area and in the area beyond as well. The activity against *Staphylococcus aureus* outlasts many washings.

It is an important advantage of the germicides of this invention that they have affinity for fibers when applied from an aqueous bath at even slightly elevated temperatures. They have notably strong affinity for cotton and may be applied thereto at temperatures as low as those encountered in laundering operations, or at the higher temperatures normally used in dyeing operations, i.e., near the boil.

In addition to cotton, the germicides of this invention have affinity for other fibers such as nylon, acetate and the like when applied as described above.

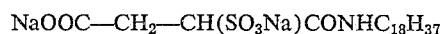
The compounds of this invention are compatible with all types of non-ionic and anionic detergents with which they form the germicidal compositions of this invention. During the process of laundering therewith, the germicide becomes attached to the fiber thus rendering it sterile for long periods. Detergent compositions having from about 0.1 to 5.0% germicide on the weight of the detergent supply an adequate amount of germicide to the fabric in normally used concentrations of detergent. When it is desired to use either greater or lesser concentrations of detergent, the concentration of the germicide may be adjusted to between 0.05% and 0.5% owf (on the weight of the fiber).

Organic anionic detergents which may be employed to formulate the compositions of this invention include alkali metal fatty acid soaps, such as sodium and potassium salts of higher fatty acids such as, stearic, oleic, linoleic, ricinoleic, palmitic, myristic, lauric and capric acids and mixtures thereof. These salts may be in their pure state or mixed, and, in the form of kettle soaps derived from the saponification of animal or vegetable fats and oils such as lard, tallow, coconut oil, babassu oil, olive oil, castor oil, cotton seed oil, and the like; and, in addition, the well known surface-active alkali metal sulfonates and sulfates. The latter may be employed as the sole detergent base or in admixture with alkali metal fatty acid soaps, as for example, 1 part of fatty acid soap to 0.5 to 2 parts by weight of the surface active

alkali metal sulfonate or sulfate or mixture thereof. A preferred type within this class is the long chain alkyl-arylsulfonates, i.e., those wherein the alkyl group is straight or branched and contains from 8-22 carbon atoms, but preferably 10-16 carbon atoms, examples of which are octyl, decyl, dodecyl, pentadecyl, hexadecyl, octadecyl, mixed long chain alkyls derived from long chain fatty acids such as the lauryl radical, cracked paraffin wax olefins, polymers of low mono-olefin such as the tetramer propylene and the like; and wherein the aryl radical is derived from benzene, toluene, xylene, phenol, the cresols, naphthalene and the like. Specific examples of these comprise sodium decylbenzene sulfonate, sodium dodecylbenzene sulfonate, sodium laurylbenzene sulfonate, and sodium hexadecylbenzene sulfonate. Other sulfonate surface active agents are contemplated also, as for example, the long chain alkyl sulfonates such as sodium hexadecylsulfonate and sodium octadecylsulfonate.

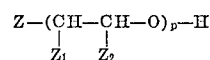
The well known anionic sulfate detergents having 12-26 carbon atoms, particularly those having an acyl radical of about 8-22 carbon atoms, may be employed herein. These include sulfuric acid esters of polyhydric alcohols incompletely esterified with fatty acids, e.g., sodium coconut oil monoglyceride monosulfate, sodium tallow diglyceride monosulfate, the pure and mixed alkyl sulfates, and higher sulfates such as sodium lauryl sulfate and sodium cetyl sulfate.

Additional anionic surface active sulfonates and sulfates contemplated by this invention are the sulfonated and sulfated alkyl acid amides (e.g., Igepon T of the formula $C_{17}H_{35}CONHCH_2CH_2SO_3Na$) and sulfated and sulfonated esters (e.g., Igepon AT of the formula $R-COO-CH_2-SO_3Na$ wherein R is an alkyl radical containing from 12-18 carbon atoms), sodium salt of the bisulfate of a dialkyl dicarboxylate, the sodium salt of the sulfonic acid derivative of a dialkyl dicarboxylate, sodium sulfosuccinated esters such as



and the like.

In addition to anionic surface active agents, non-ionic surface active agents are useful in the germicidal compositions of this invention. Non-ionic surface active agents which may be used are generally viscous, wax-like, water-soluble surface active substances containing a polyglycol ether group of the structure



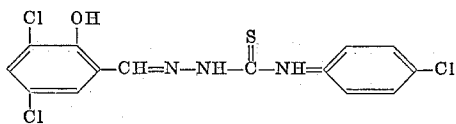
wherein Z_1 and Z_2 are hydrogen or a lower alkyl, p is an integer greater than three and Z is the residue of a monomeric organic compound having an active hydrogen, as for example, an alcohol, a phenol, an amide, a primary amine (e.g., stearyl and lauryl amines), a secondary amine (e.g., dibutylamine), a carboxylic acid or the like. These non-ionic detergents are well known (e.g., U.S. 1,970,578 and U.S. 2,213,477) and may be typified by polyalkylene oxide derivatives (e.g., polyethylene oxide, polypropylene oxide, polybutylene oxide) of water-insoluble high fatty acids, such as lauric, oleic, palmitic and stearic and the like. Alkylene oxide derivatives of such water-insoluble organic hydroxy compounds as the fatty alcohols, phenols (particularly those having alkyl groups such as either isooctyl-, *t*-butyl, trisopropyl-, nonyl-, dodecyl- or octadecyl-phenol), or aralkyl alcohols (e.g., benzyl alcohol) and the like are likewise useful. They may also be exemplified by the polyalkylene oxide derivatives of such amines as stearyl, lauryl, dicyclohexyl, dibutylamine and the like.

A mixture of an anionic and a non-ionic surface active agent may be used in preparing a germicidal composition of this invention.

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This invention is further illustrated by the following examples in which parts are by weight unless otherwise specified.

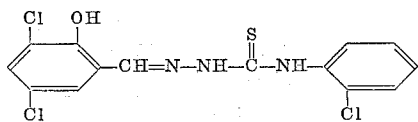
EXAMPLE 1



Six and one-half parts of 3,5-dichlorosalicylaldehyde is dissolved in 50 parts by volume of boiling alcohol and the solution is added to a hot slurry of 6.3 parts of 4-(p-chlorophenyl)-3-thiosemicarbazide in 200 parts of alcohol. A clear solution forms temporarily. On stirring, a granular precipitate forms which is isolated by filtration and dried. The product is recrystallized by dissolving in boiling methoxyethanol and adding an equivalent volume of water. The product is isolated by filtration and dried.

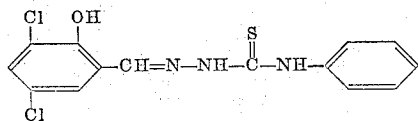
Similarly, when 4-(p-methoxyphenyl)-3-thiosemicarbazide is used in place of the 4-(p-chlorophenyl)-3-thiosemicarbazide in equivalent amounts, the corresponding methoxy derivative is obtained.

EXAMPLE 2



Six and one half parts of 3,5-dichlorosalicylaldehyde is dissolved in 50 parts by volume of boiling alcohol and the solution added to a hot solution of 6.3 parts of 4-(o-chlorophenyl)-3-thiosemicarbazide in 150 parts by volume of alcohol. A slurry forms which on stirring and standing, thickens. The product is isolated by filtration and recrystallized from methoxyethanol. It is filtered and dried.

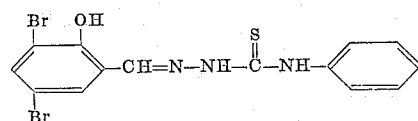
EXAMPLE 3



Nine and one half parts of 3,5-dichlorosalicylaldehyde is dissolved in 50 parts by volume of boiling alcohol and added to a hot solution of 10 parts of 4-phenyl-3-thiosemicarbazide in 100 parts by volume of alcohol. A slurry forms which is stirred occasionally and allowed to stand. The product is isolated by filtration and recrystallized from 1,200 parts by volume of alcohol. The product is isolated by filtration and dried.

Similarly, if the 4-phenyl-3-thiosemicarbazide is replaced by equivalent quantities of 4-o-tolyl-3-thiosemicarbazide, 4-o-methoxyphenyl-3-thiosemicarbazide, 4-(β-naphthyl)-3-thiosemicarbazide, 4-(3,4-dichlorophenyl)-3-thiosemicarbazide and 4-(2,4,6-trichlorophenyl)-3-thiosemicarbazide, the corresponding 4-o-tolyl, 4-o-methoxyphenyl, 4-(β-naphthyl), 4-(3,4-dichlorophenyl), and 4-(2,4,6-trichlorophenyl) derivatives of 3,5-dichlorosalicylaldehyde are respectively obtained.

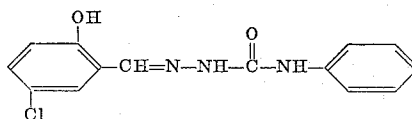
EXAMPLE 4



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8.2 parts of 4-phenyl-3-thiosemicarbazide is dissolved in 60 parts by volume of boiling alcohol and added to a hot solution of 16.7 parts of 3,5-dibromosalicylaldehyde in 120 parts by volume of alcohol. A paste forms which is stirred occasionally and allowed to stand. The product is filtered off and dissolved in 1,500 parts by volume of hot alcohol. On standing and cooling to room temperature, the product precipitates and it is isolated by filtration and dried.

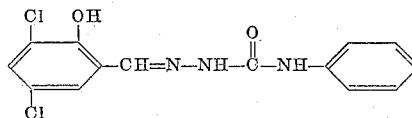
EXAMPLE 5



4.7 parts of 5-chlorosalicylaldehyde is dissolved in 20 parts by volume of alcohol. This solution is added to a hot solution of 3.78 parts of 4-phenylsemicarbazide in 40 parts by volume of alcohol. After standing and cooling, the product is filtered and dried in vacuum. It is then purified by refluxing with 100 parts by volume of alcohol. The mixture is then cooled, filtered and dried in a vacuum oven.

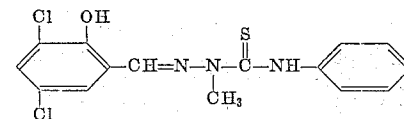
When 4-phenyl-3-thiosemicarbazide in an equivalent amount is used in place of the semicarbazide used above, the corresponding thiosemicarbazone is obtained.

EXAMPLE 6



A solution of 5.73 parts of 3,5-dichlorosalicylaldehyde in 20 parts by volume of alcohol is added to a solution of 3.78 parts of 4-phenylsemicarbazide in 40 parts by volume of alcohol. The precipitate which forms upon standing and cooling, is filtered and dried. The cake is refluxed with 100 parts by volume of alcohol, and cooled. The product is separated by filtration and dried in a vacuum oven.

EXAMPLE 7



A hot solution of 5.73 parts of 3,5-dichlorosalicylaldehyde is added to a hot solution of 4.53 parts of 4-phenyl-2-methyl-3-thiosemicarbazide in 40 parts by volume of alcohol. After standing and cooling, the precipitated product is isolated by filtration, dried and recrystallized from alcohol.

EXAMPLE 8

A series of products similar to the foregoing is prepared by the general method given below. Table I shows the combinations used and the germicidal activity of the products obtained.

0.05 mole of a 4-aryl-3-thiosemicarbazide or 4-aryl-3-semicarbazide is dissolved in the minimum amount of boiling alcohol, and this solution is added to a hot alcoholic solution of 0.06 mole of the salicylaldehyde. On standing and cooling, the product precipitates. It is filtered and washed with alcohol. It is then purified by about 2 hours digestion with 200 ml. of refluxing alcohol. It is filtered hot and dried.

The new halogenated salicylaldehyde derivatives are padded on cotton, applied to the cloth from a detergent

bath, and tested for germicidal activity by procedures outlined immediately following Table I below:

TABLE I

No.	Reactants condensed	Activity versus <i>Staph. aureus</i>			
		Padding		Detergent bath	
		Percent weight (OWF)*	Zone (mm.)	Percent weight (OWF)	Zone (mm.)
(a)-----	3,5-dibromosalicylaldehyde, 4-(p-chlorophenyl)-3-thiosemicarbazide.	0.5	15.3----	{ 0.5 0.1 0.05	13.3. 12.6. C.
(b)-----	3,5,6-trichlorosalicylaldehyde, 4-phenyl-3-thiosemicarbazide.	0.5	14.9----	{ 0.5 0.1	12.6. P.
(c)-----	3,5-dichlorosalicylaldehyde, 4-(p-tolyl)-3-thiosemicarbazide.	0.5	19.0----	{ 0.5 0.1	14.2. 12.3. 13.3.
(d)-----	3,5-dichlorosalicylaldehyde, 2,4-diphenyl-3-thiosemicarbazide.	0.5	12.0----		
		0.5	12.4p----		
(e)-----	3,5-dichlorosalicylaldehyde, 4,4-diphenylsemicarbazide.	0.5	12.0p----		
(f)-----	3,5-dichlorosalicylaldehyde, 4-(α -naphthyl)-3-thiosemicarbazide.	0.5	16.8----	{ 0.5 0.1	12.4. P.

*On weight of the fiber.

EXAMPLE 9

A. Procedure for padding on cotton and washing padded fabrics

To 0.588 g. of the compound to be tested is added 99.412 g. of dimethylformamide to give a total of 100 g. of solution. The solution is placed in a pad box. One yard of 80 x 80 cotton percale 16 inches wide and weighing about 38-40 g. is dipped once through the pad box containing the solution and then nipped once through 18-inch rollers of a microset padder adjusted at 25 pounds pressure. The takeup of the solution is 85%. The fabric is then pinned taut on a frame and placed in an oven circulating hot air at 225° F. for 2 minutes which completely dries it. It is then subjected to the procedure given in Part "C" for determining its germicidal activity.

To determine the durability of the attachment of the germicidal compound, a 20" x 20" piece of padded 80 x 80 cotton is put through five or more washing cycles. Each cycle consists of the following operation:

A commercial automatic washing machine having capacity for a 6-lb. load is filled with water at 140° F. and sufficient neutral soap added to make a 0.1% soap solution. The volume of water is about 15 gallons. A 6-lb. load of cotton, including the test sample of 80 x 80 padded cotton, is added and a washing period of 20 minutes ensues. This is followed by a 10-minute rinse period using water at 120° F. and then another rinse period of five minutes using water at 100° F. After that, the load is spun to semi-dryness. Total cycle is about 40 minutes.

B. Procedure for applying germicide from a detergent bath

50 mg. of the germicide is dissolved in 1 ml. of dimethylformamide. One drop of Triton X-100 (Reg. T.M.), a wetting and dispersing agent which is an alkyl aryl polyether alcohol, is added and the solution made up to 100 ml. with distilled water. This gives a stock solution of the germicide for application to the fabrics.

For a 0.05% OWF application on 80 x 80 cotton fabric, 5 ml. of the stock solution is added to 50 ml. of a 0.50% solution of an anionic detergent containing 35% of sodium dodecyl benzene sulfonate, and 40% of sodium

tripolyphosphate plus inert constituents. This mixture is made up to a total of 100 ml. with distilled water. A 5-gram piece of 80 x 80 cotton is entered and treated for 20 minutes at 130° F. It is then rinsed three times in distilled water having a temperature of 80-90° F. and air-dried at room temperature.

C. Procedure for evaluation of germicides

A 20 ml. portion of sterile melted agar is added to a Petri dish and allowed to solidify. Another bottle containing 100 ml. of sterile melted agar is cooled to 115-120° F. and inoculated with 0.25 ml. of an overnight bacterial culture of *Staphylococcus aureus* grown in a nutrient agar broth. 4 ml. of the inoculated agar is uniformly spread over the hard base layer in the Petri dish and allowed to solidify on a level surface. This agar dish is then ready to receive test samples of fabric. At least two 11.5 mm. diameter discs of the 80 x 80 fabric having germicide applied from a detergent bath or padded on, are punched out of the test fabric. These discs are then carefully placed on the agar with forceps, about 1" apart. The Petri dishes are covered and kept at room temperature for 2 hours. The test discs are then removed with forceps and the dish is allowed to incubate for a total of 16-20 hours at 100° F. Where bacterial growth has taken place, the agar will be opaque. The sites of those discs having effective germicidal action, will remain clear. These clear areas contain no bacterial growth and are called zones of inhibition.

When no zone of inhibition occurs outside the area of the discs, i.e., outside of the 11.5 mm. area, the activity within this area is noted. The scale set up to describe this condition is as follows:

"C"—means complete inhibition, a clear zone in the area in contact with the cloth disc.
 "P"—means partially or nearly complete inhibition in the area under the disc.
 "N"—means little or no inhibition; opacity is similar to that of the uninhibited growth.
 "S"—means 10-25% inhibition.
 "Vs"—means 0.10% inhibition.

Where the area of inhibition extends beyond the 11.5 mm. diameter and is greater than that of the disc, the diameter of the inhibition area is measured and recorded in millimeters. Thus, 12.0 means that the area is clear under the 11.5 mm. disc plus an extra 0.5 mm. clarity. 12.0p means that the area is partially inhibited under the 11.5 mm. disc plus a partially inhibited extra 0.5 mm. area in diameter. A single measurement is reported after averaging the measurements, provided they are within 1.5 mm. of each other. If they are more than 1.5 mm. apart, the reading for each disc is recorded separately.

EXAMPLE 10

Compounds of the foregoing examples were tested for germicidal activity on cotton using the above described padding and "detergent bath" techniques A and B, respectively, of Example 9. The following table records the results.

TABLE II

Compound of—	Concentration, percent (OWF)	Germicidal activity vs. <i>Staph. aureus</i>	
		Padding activity (mm.)	Detergent bath—5 washings activity (mm.)
Example 1-----	0.5	17.0-----	P-C; 12.0p.
Example 3-----	0.5	21.2-----	P; 12.3p.
Example 4-----	{ 0.5	18.4-----	12.8; P-C; 12p.
Example 5-----	1.0	18.7-----	
Example 6-----	0.5	P-C; 12.0p-----	
Example 7-----	0.5	14.5-----	
	0.5	12.3; 13.4p-----	

EXAMPLE 11

Cotton treated by the detergent bath method, Example 9B, with varying concentrations of the compound of Example 3 shows the following activity against *Staph. aureus*:

TABLE III

Conc., percent (OWF)	Activity vs. <i>Staph. aureus</i> (mm.)
0.5	15.3.
0.1	C; 12.7p.
0.1	P; 12.0p.
0.08	P-C; 12.0p.

EXAMPLE 12

A stock solution containing the product of Example 3 is prepared by the method of Example 9B. For 0.1% and 0.5% applications, water to make 100 ml. is added to 10 ml. and 50 ml. portions, respectively. No detergent solution is used. A 5-g. sample of fabric is entered and the application procedure continued as in Example 9B. The dried treated fabric is tested for activity against *Staph. aureus*, giving the results shown below:

TABLE IV

Percent applied (OWF) and fabric used	Germicidal activity (mm.)
0.1% nylon-----	(13.6. 12.3.
0.5% nylon-----	(15.8. 15.0.
0.1% acetate-----	(14.0. 12.6; 13.5p.
0.5% acetate-----	15.3.

EXAMPLE 13

Stock solutions of the compounds of Examples 3 and 4 are prepared as in Example 9B, and each is added to an anionic detergent comprising 17% of an alkyl benzene sulfonate, an alcohol sulfate and 40% sodium tripolyphosphate plus inert ingredients. The cotton treated by the detergent bath method with these solutions exhibits the following activity:

TABLE V

Compound applied	Conc., percent (OWF)	No. of treatment	Activity vs. <i>Staph. aureus</i> (mm.)
Example 4-----	0.5	1	14.7.
	0.1	1	C; 12.3.
	0.05	1	C; 12.0p.
	0.05	5	P-C; 12.0p.
	0.05	10	C; 12.1p.
Example 3-----	0.5	1	16.1.
	0.1	1	13.1; 13.9.

EXAMPLE 14

A mixture of one part of the product of Example 1 and 99 parts of an anionic detergent comprising sodium dodecyl naphthalenesulfonate is prepared by dissolving the product of Example 1 in a minimum amount of alcohol and adding the solution to a solution of the detergent in a minimum of water. The resulting mixture is then dried in a vacuum. The product can be used directly as the detergent in a laundering operation to produce sterile germicidally treated textiles.

When the detergent above is replaced with a mixture of the alkali metal salts of fatty acids (45% oleic and linoleic, 30% palmitic, 10% stearic, 15% lower fatty

acids) a composition suitable for use in bar soap, is obtained.

The proportion of the product of Example 1 to the detergent can be varied from 1 part to 999 parts of detergent to 5 parts to 95 parts of detergent, to give compositions of proportional potency in germicidal activity.

EXAMPLE 15

The procedure of Example 16 is followed using a non-ionic detergent comprising a polyoxyethylene ester of stearic acid in place of the anionic detergent. A similarly usable product is obtained.

When the products of Examples 2, 3, 4, 5, 6, and 7 are used in place of that of Example 1, similar products are also obtained.

When other non-ionic agents such as polyoxyethylene ethers are used in place of the above ester, similar products are obtained.

EXAMPLE 16

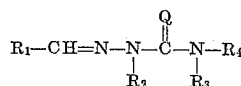
To hot soap, made by saponifying a mixture of 80 parts of tallow and 20 parts of coconut oil with caustic soda lye and evaporating, is added with crutching,

0.2 part of sodium chloride
0.25 part of titanium dioxide
0.004 part of F.D. & C. Red 4, Colour Index 14700
1.0 part of 70% soap grade geraniol
0.1 part of the product of Example 3

Crutching is continued until a homogeneous mixture is obtained. The mixture is poured into trays, cut into strips and fed into a bar cutting and moulding machine. A germicidal bar soap is thus obtained.

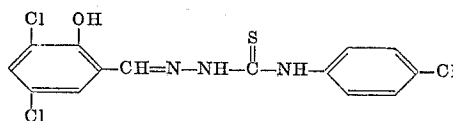
I claim:

1. A compound of the formula:

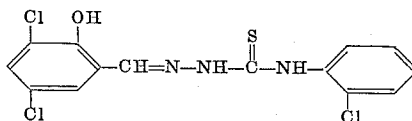


wherein R_1 is a halogenated ortho-hydroxy aryl radical of less than three 6-membered rings, in which the halogen has an atomic number between 16 and 36, R_2 is a member selected from the group consisting of hydrogen and lower alkyl, R_3 is selected from the group consisting of hydrogen, lower alkyl, cyclohexyl, monocyclic ar(lower alkyl) and monocyclic aryl, R_4 is aryl of less than three 6-membered rings, and Q is selected from the group consisting of O and S; and each aryl moiety in the compound if it is substituted beyond the required substitution in R_1 has the substituents chosen from the group consisting of lower alkyl, lower alkoxy, chloro, bromo and nitro.

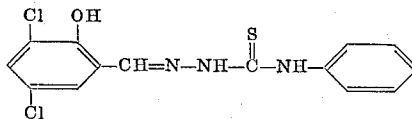
2. The compound of the formula:



3. The compound of the formula:

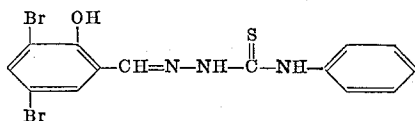


4. The compound of the formula:

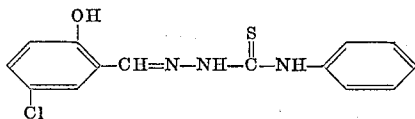


11

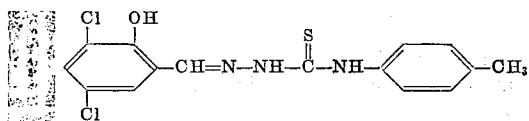
5. The compound of the formula:



6. The compound of the formula:

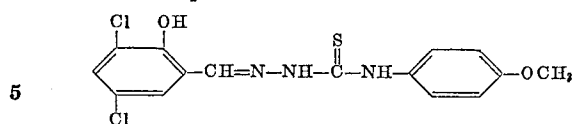


7. The compound of the formula:



12

8. The compound of the formula:



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IRVING MARCUS, *Primary Examiner.*MORRIS O. WOLK, JOHN D. RANDOLPH, *Examiners.*

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,182,082

May 4, 1965

Walter J. Sydor

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 4, line 14, for "doecylbenzene" read -- dodecylbenzene --; column 7, TABLE I, third column, line 5 thereof, strike out "0.5"; column 8, line 42, "0.10%" read -- 0-10% --.

Signed and sealed this 5th day of October 1965.

SEAL)

Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents