

1

3,177,115

ANTISEPTIC COMPOSITIONS

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This invention relates to antiseptic compositions having synergic effect. In one of its aspects this invention relates to improved germicidal cleansing compositions containing as their essential germicidal ingredients a synergistic combination of either an unalkylated or alkylated polyhalobisphenol and 3,4,4'-trichlorocarbanilide or its position isomer 3,3',4-trichlorocarbanilide.

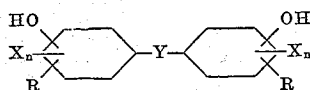
This application is a continuation-in-part of our copending application Serial No. 741,455, filed June 12, 1958, now abandoned.

The popularity of germicidal cleansing compositions for laundry and toilet use has increased tremendously over the past few years. In fact, it has been estimated that better than 20% of bar soap sales now are of products containing a germicidal agent, and this percentage is steadily increasing. There are a number of germicidal agents currently in use, but the unalkylated halogenated bisphenols appear to be the most widely accepted because of their activity, compatibility and commercial availability. One of the compounds of this class is 2,2'-dihydroxy - 3,5,6,3',5',6' - hexachlorodiphenyl methane, commonly known as hexachlorophene, which is now in widespread commercial use. Another example is 2,2'-dihydroxy - 3,5,3',5' - tetrachlorodiphenyl sulfide, commonly known as bithionol. The action of halogenated bisphenols such as hexachlorophene when incorporated in soap, the proportions required, and other pertinent information, is set out more fully in U.S. Patent No. 2,535,077 to Kunz et al.

There are certain inherent disadvantages to the use of both unalkylated and alkylated halogenated bisphenols. For example, they are photo-sensitive and tend to cause discoloration in the finished product upon exposure to light. Hence, they cannot be used in a pure white soap. Also, they are somewhat toxic and present a potential hazard to domestic animals which are prone to eat things, even soap. Therefore, it would be desirable to diminish these disadvantages without adversely affecting their germicidal activity. From a different point of view, it would also be worthwhile if these disadvantages could be maintained at their present level and the germicidal activity of the unalkylated and alkylated halogenated bisphenols increased. We have discovered that these objects can be accomplished through the production of a synergic effect.

In accordance with the present invention, the germicidal activity of unalkylated and alkylated halogenated bisphenols in antiseptic compositions is enhanced, synergized or potentiated by the incorporation therewith of 3,4,4'-trichlorocarbanilide or its position isomer 3,3',4-trichlorocarbanilide. The products of the invention, therefore, are antiseptic compositions containing as their essential active ingredients a synergistic combination of either an unalkylated or alkylated halogenated bisphenol and 3,4,4' - trichlorocarbanilide or its position isomer 3,3',4-trichlorocarbanilide.

For the purposes of this invention, any suitable unalkylated or alkylated polyhalobisphenol may be used as one of the ingredients. The unalkylated and alkylated polyhalobisphenols may be represented according to their chemical structure as follows:



2

wherein X represents a halogen such as chlorine or bromine, n represents an integer of from 1 to 3, Y represents a divalent radical including alkylene radicals having from 1 to 4 carbon atoms such as $-\text{CH}_2-$,

5 $-\text{CH}_2\text{CH}_2-$, $-\text{CH}(\text{CH}_3)-$, $-\text{C}(\text{CH}_3)_2-$
 $-\text{CH}_2\text{CH}_2\text{CH}_2-$, etc.; halo-substituted alkylene radicals having 1 to 4 carbon atoms such as $-\text{CHCl}-$,
10 $-\text{CHBr}-$, $-\text{CHClCHCl}-$, $-\text{CH}(\text{CCl}_3)-$
 $-\text{CH}(\text{CBr}_3)-$, etc.; and $-\text{S}-$; and R in the case of alkylated polyhalobisphenols is an alkyl group containing from 1 to 4 carbon atoms.

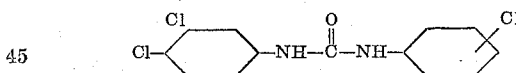
The preferred compounds are symmetrical in structural configuration. Specific examples of the unalkylated polyhalobisphenols include

15 2,2'-dihydroxy-3,5,6,3',5',6'-hexachlorodiphenyl methane,
2,2'-dihydroxy-3,5,3',5'-tetrachlorodiphenyl methane,
20 2,2'-dihydroxy-4,5,4',5'-tetrachlorodiphenyl methane,
2,2'-dihydroxy-3,4,3',4'-tetrachlorodiphenyl methane,
2,2'-dihydroxy-5,5'-dibromodiphenyl methane,
2,2'-dihydroxy-3,5,3',5'-tetrachlorodiphenyl sulfide, and
2,2'-dihydroxy-5,5'-dichlorodiphenyl sulfide.

Specific examples of the alkylated halogenated bisphenols include

2,2'-dihydroxy-3,3'-dimethyl-5,5'-dichlorodiphenyl sulfide,
30 2,2'-dihydroxy-3,3'-dimethyl-5,5'-dichlorodiphenyltrichloroethane,
2,2'-methylene-bis(4-chloro-6-isopropylphenol),
2,2'-methylene-bis(6-sec-butyl-4-chlorophenol),
2,2'-ethyldiene-bis(4-chloro-6-isopropylphenol),
35 2,2'-ethyldiene-bis(6-sec-butyl-4-chlorophenol),
2,2'-isopropylidene-bis(4-chloro-6-isopropylphenol), and
2,2'-isopropylidene-bis(6-sec-butyl-4-chlorophenol).

Used in conjunction with the unalkylated and alkylated halogenated bisphenols in the present invention are polyhalocarbanilides, 3,4,4'-trichlorocarbanilide or its position isomer 3,3',4-trichlorocarbanilide in particular, which can be represented by the following structural formula:



It has been found that when the unalkylated or alkylated halogenated bisphenols and the 3,4,4'-trichlorocarbanilide or 3,3',4-trichlorocarbanilide, as illustrated above, are used together in an antiseptic composition a germicidal effect is achieved which is greater than the mere total of the individual effects of the individual ingredients. This has importance in cases where the activity of the bisphenol is desired to be increased without employing higher concentrations, and in other cases, it assumes an even greater importance from an economic standpoint, since the presence of the trichlorocarbanilide enables a reduction in the total concentration of the germicidal agent while at the same time retaining the desired level of germicidal effect.

What the actual mechanism of the potentiating or synergistic effect is, we are unable to explain. The invention relates to the synergistic cooperation of these two types of compounds when used in minor proportions in antiseptic compositions, especially antiseptic detergent compositions, and the discovery that this synergistic phenomenon occurs even at the high pH conditions existing in soap and detergent formulations provides one of the important phases of the present invention.

Relatively small amounts of the bisphenols and the trichlorocarbanilides are sufficient for the increased germicidal effect in the present invention. Satisfactory results

can be obtained when the combined weights of the two agents are from 0.05% to 5% of the total weight of the composition. The objects of the invention may be achieved when the weight of the bisphenol is about 0.1% to 3% and the trichlorocarbanilide is about 3% to about 0.1% of the soap or detergent weight. The preferred range is a weight concentration of about 0.25% to 1.75% of the bisphenol and about 1.75% to 0.25% of the trichlorocarbanilide, and an excellent product is one containing soap and about 1% of each of the bisphenol and the trichlorocarbanilide. It will be understood that even concentrations below the ranges just set out will provide some degree of germicidal effect and a substantially higher concentration than those referred to will provide satisfactory results, although there are certain practical considerations such as the cost of the bisphenols and a certain impairment in the detergent properties, which limits the desirability of greater amounts of the germicidal composition in the soap.

As indicated above, the ratio of the preferred range of the bisphenols to the trichlorocarbanilide is about 1-7 of the bisphenol to about 7-1 of the trichlorocarbanilide, the parts being by weight. In other words, in a soap containing a germicidal concentration of hexachlorophene or bithionol, the trichlorocarbanilide is preferably used in the proportion of 1-7 parts to 7-1 parts of the hexachlorophene or bithionol.

The term "soap" refers to the water-soluble ammonium, metallic, or organic base salts of various fatty acids, which are chiefly lauric, oleic, stearic, and palmitic acids. As used in this description, the term is intended to cover all products in which soap is a major constituent, for example, bar, flake, powdered, soft and liquid soaps; shaving creams, toothpaste, cleansing creams, etc.

The invention also contemplates the use of anionic-type and non-ionic-type synthetic detergents in place of the soap. The anionic-type synthetics suitable for use in the invention can be described as those detergents having pronounced cleansing power and including in their molecular structure an alkyl radical containing from 6 to 18 carbon atoms and a sulfonic acid or sulfuric acid ester radical. Either organic base, ammonium, sodium or potassium salts of the anionic-type detergents can be used. The main types of detergents falling within this category are alkyl-aryl sulfonates, such as sodium or potassium dodecyl benzene sulfonate, sodium or potassium octadecyl benzene sulfonate, and sodium or potassium octyl naphthalene sulfonate; the alkyl sulfates, such as sodium or potassium salts of dodecyl, hexadecyl, and octadecyl sulfates; the sulfonated fatty acid amides, such as sodium or potassium salts of the oleic acid amide of methyl taurine; and the sulfonated monoglycerides such as the mono-coconut oil fatty acid ester of 1,2-hydroxypropane-3-sodium sulfonate.

The non-ionic-type synthetic detergents suitable for use in the invention may be described as those detergents which do not ionize in solution but owe their water-solubility to un-ionized polar groups such as hydroxyl or ether linkages. The main types of detergents falling within this category are the polyoxyethylene ethers of the higher fatty alcohols and alkyl phenols; the polyethylene glycols of fatty acids; fatty alkylol amide condensation products; polymers of ethylene and propylene oxides; compounds formed by the addition of propylene oxide to ethylene diamine, followed by the addition of ethylene oxide; fatty acid ethylene oxide condensation products; condensation products of ethylene oxide and a fatty acid ester of a polyhydric alcohol or sugar; and the detergents prepared by heating together a higher fatty acid with a diethanolamine. Some examples of synthetic non-ionics suitable for the purposes of this invention are ethylene oxide-tall oil fatty acid reaction products; iso-octyl phenol-ethylene oxide reaction products; propylene oxide-ethylene oxide reaction products; and combinations of iso-octyl phenol-ethylene oxide with coconut oil fatty acid-ethylene oxide reaction products.

The synergistic combinations of either the unalkylated or alkylated halogenated bisphenol and the 3,4,4'-trichlorocarbanilide or its position isomer 3,3',4-trichlorocarbanilide can be added to the soap or the detergent by any suitable method which results in a uniform distribution of the additives throughout the entire mass. A highly satisfactory dispersion method of carrying out the addition step is described more fully in copending application Serial No. 263,302, filed December 26, 1951, now abandoned.

Specific examples illustrating the invention are set out as follows:

EXAMPLE I

Antiseptic detergent compositions exemplary of the present invention were prepared by intimately mixing the ingredients listed in Table I below to form a composite containing 2% by weight "active ingredient."

Table I

Composition	A	B	C	D	E
Neutral white toilet soap containing about 20% by weight of sodium coco soap and 80% by weight of sodium tallow soap	98	98	98	98	98
2,2'-dihydroxy-3,5,6,3',5',6'-hexachlorodiphenyl methane	2				1
2,2'-dihydroxy-3,5,3',5'-tetrachlorodiphenyl sulfide		2		1	
3,4,4'-trichlorocarbanilide			2	1	1

Aliquots of each of the above-described compositions containing 2% by weight "active ingredient" were added to nutrient agar medium so as to give in each instance a concentration of 0.125 part per million of "active ingredient" in agar. The agar in each case was then poured into a Petri dish, allowed to harden and then streaked with a 24-hour old broth culture of *M. pyogenes* var. *aureus* diluted 1-10. The incubation in each case was at a temperature of 37° C. The degree of growth after a period of 48 hours is set forth in Table II, as follows:

Table II

Composition	A	B	C	D	E
Period of Incubation	48	48	48	48	48
Amount of Growth	3+	3+	3+	1+	1+

Legend:

- = No growth.
- 1+ = Very slight growth.
- 2+ = Light to moderate growth.
- 3+ = Normal heavy growth.

EXAMPLE II

Soap compositions were prepared to incorporate 2% by weight of germicidal ingredients in each sample. Compositions of the samples were:

Table I

Composition	A	B	C
Neutral toilet soap containing about 30% by weight of sodium coco soap and 80% by weight of sodium tallow soap	98	98	98
2,2'-dihydroxy-3,3'-dimethyl 5,5'-dichlorodiphenyl sulfide	2		1
3,4,4'-trichlorocarbanilide (TCC)		2	1

Aliquots of each of the above-described compositions containing 2% by weight of active ingredients were added to nutrient agar medium so as to give in each instance a concentration of 0.15 p.p.m. of "active ingredient" in the agar. The agar in each case was poured into a Petri dish, allowed to harden and then streaked with a 24-hour broth culture of *M. pyogenes* var. *aureus* diluted

1-10. The incubation period in each case was made at 37° C. for 48 hours. The degree of growth is set out in Table II below:

Table II

Composition	A	B	C
Growth.....	3+	3+	½+

Legend:

3+ = Normal heavy growth.
2+ = Moderate growth.
1+ = Light growth.
½+ = Extremely light growth.

Thus it may be seen that true synergism exists in the test described above.

EXAMPLE III

Both individual germicides and combinations of germicides were incorporated in a soap containing 20% sodium coco soap and 80% sodium tallow soap, a non-ionic synthetic detergent and an anionic synthetic detergent, at a total concentration of 1% basis soap and 1% detergent solution prepared. Aqueous solutions of the individual germicides were also prepared at a concentration of 100 p.p.m. and further diluted to 10 p.p.m. The 1% detergent solutions were also diluted with distilled water to 10 p.p.m. total germicide. Aliquot amounts of these solutions were then added to liquid nutrient agar so as to give the concentrations of the germicide in agar in Table I below. Plates were poured, allowed to harden and streaked with a 24-hour broth culture of *M. pyogenes* var. *aureus* FDA strain 209. The plates were incubated 48 hours at 37° C. and the amount of growth in the plates noted. The results are given in Table I as follows:

Table I

Amount of growth (*M. pyogenes*) on agar plates with agar containing aliquots of the germicides incorporated in the following agents:

Total Germicide Basis Agar, p.p.m.	Water				Soap				Nonionic Detergent				Anionic Synthetic Detergent			
	0.6	0.4	0.2	0.1	0.6	0.4	0.2	0.1	0.6	0.4	0.2	0.1	0.6	0.4	0.2	0.1
TCC.....	---	3+	3+	3+	---	1+	3+	3+	---	0	0	2+	---	0	3+	3+
G-11.....	---	0	2+	3+	---	0	2+	3+	---	0	0	2+	---	0	2+	3+
TCC+G-11.....	---	0	0	0	---	0	0	3+	---	0	0	1+	---	0	0	0
G-5.....	2+	3+	3+	3+	---	3+	3+	3+	---	0	3+	3+	---	2+	3+	3+
TCC+G-5.....	0	0	0	2+	---	0	1+	3+	---	0	0	1+	---	0	1+	3+
G-11-S.....	1+	3+	3+	3+	---	3+	3+	3+	---	1+	2+	3+	---	2+	3+	3+
TCC+G-11-S.....	0	0	1+	3+	---	0	2+	3+	---	0	0	1+	---	0	1+	3+
Bithionol.....	3+	3+	3+	3+	---	2+	3+	3+	---	1+	2+	3+	---	2+	3+	3+
TCC+Bith.....	0	0	0	3+	---	0	0	1+	---	0	0	1+	---	0	0	3+
S-1.....	3+	3+	3+	3+	---	3+	3+	3+	---	2+	3+	3+	---	2+	3+	3+
TCC+S-1.....	0	0	3+	3+	---	0	1+	2+	---	0	0	1+	---	0	2+	3+
TCC-A.....	---	0	3+	3+	---	0	0	3+	---	0	0	2+	---	0	1+	3+
G-11.....	---	---	2+	3+	---	---	2+	3+	---	0	0	2+	---	0	2+	3+
TCC-A+G-11.....	---	0	0	0	---	0	0	1+	---	0	0	0	---	0	0	2+
G-5.....	2+	3+	3+	3+	---	3+	3+	3+	---	2+	3+	3+	---	2+	3+	3+
TCC-A+G-5.....	0	0	0	3+	---	0	0	1+	---	0	0	0	---	0	0	3+
G-11-S.....	1+	3+	3+	3+	---	3+	3+	3+	---	1+	2+	3+	---	2+	3+	3+
TCC-A+G-11-S.....	0	0	0	2+	---	0	0	1+	---	0	0	1+	---	0	0	3+
Bithionol.....	1+	3+	3+	3+	---	2+	3+	3+	---	1+	2+	3+	---	---	3+	3+
TCC-A+Bith.....	---	0	0	0	---	0	0	1+	---	0	0	0	---	0	0	3+
S-1.....	3+	3+	3+	3+	---	3+	3+	3+	---	1+	3+	3+	---	---	3+	3+
TCC-A+S-1.....	0	0	2+	3+	---	0	0	2+	---	0	0	1+	---	0	1+	2+

Code:

0=No growth on plates. 1=Light growth. 2=Moderate growth. 3=Normal heavy growth.

LEGEND

Materials Used:

G-11—Hexachlorophene, 2,2-dihydroxy hexachlorodiphenyl methane.
G-5—2,2'-dihydroxy tetrachlorodiphenyl methane.
G-11-S—2,2'-dihydroxy hexachlorodiphenyl sulfide.
TCC—3,4,4'-trichlorocarbaniide.
TCC-A—3,3',4'-trichlorocarbaniide.
S-1—2,2'-thiobis(dichloro dimethyl)phenol.
Soap—20% sodium coco soap, 80% sodium tallow soap.
Nonionic Detergent—Nonylphenol plus 9 moles ethylene oxide.
Anionic Synthetic Detergent—Sodium dodecylbenzene sulfonate.

EXAMPLE IV

Antiseptic detergent compositions exemplary of the present invention were prepared by intimately mixing the ingredients listed in Tables I, II and III below to form a composite containing 0.5%, 1.0% and 3.0% respectively by weight "active ingredient."

Table I

Composition	A	B	C	D	E
Neutral white toilet soap containing about 20% by weight of sodium coco soap and 80% by weight of sodium tallow soap.....	99.50	99.50	99.50	99.50	99.50
2,2'-dihydroxy-3,5,6,3',5',6'-hexachlorodiphenyl methane.....	0.50	-----	-----	0.25	-----
2,2'-dihydroxy-3,5,3',5'-tetrachlorodiphenyl sulfide.....	-----	0.50	-----	-----	0.25
3,4,4'-trichlorocarbaniide.....	-----	-----	0.50	0.25	0.25

Table II

Composition	A	B	C	D	E
Neutral white toilet soap containing about 20% by weight of sodium coco soap and 80% by weight of sodium tallow soap.....	99	99	99	99	99
2,2'-dihydroxy-3,5,6,3',5',6'-hexachlorodiphenyl methane.....	1	-----	-----	0.50	-----
2,2'-dihydroxy-3,5,3',5'-tetrachlorodiphenyl sulfide.....	-----	1	-----	-----	0.50
3,4,4'-trichlorocarbaniide.....	-----	-----	1	0.50	0.50

Table III

Composition	A	B	C	D	E
Neutral white toilet soap containing about 20% by weight of sodium coco soap and 80% by weight of sodium tallow soap.....	97	97	97	97	97
2,2'-dihydroxy-3,5,6,3',5',6'-hexachlorodiphenyl methane.....	3	-----	-----	1.50	-----
2,2'-dihydroxy-3,5,3',5'-tetrachlorodiphenyl sulfide.....	-----	3	-----	-----	1.50
3,4,4'-trichlorocarbaniilide.....	-----	-----	3	1.50	1.50

Aliquots of each of the above-described compositions containing 0.50%, 1% and 3% respectively by weight "active ingredient" were added to nutrient agar medium so as to give in each instance a test concentration of 0.125 part per million of "active ingredient" in agar. The agar in each case was then poured into a Petri dish, allowed to harden and then streaked with a 24-hour old broth culture of *M. pyogenes* var. *aureus* diluted 1-10. The incubation in each case was at a temperature of 37° C. The degree of growth after a period of 48 hours is set forth in the following tables, in which Table I-A shows the results for Table I, Table II-A shows the results as to Table II, and Table III-A shows the results as to Table III:

Table I-A

Composition	A	B	C	D	E
Period of Incubation.....	48	48	48	48	48
Amount of Growth.....	1+	1+	3+	0	0

Table II-A

Composition	A	B	C	D	E
Period of Incubation.....	48	48	48	48	48
Amount of Growth.....	2+	2+	3+	0	0

Table III-A

Composition	A	B	C	D	E
Period of Incubation.....	48	48	48	48	48
Amount of Growth.....	2+	2+	3+	1+	1+

Legend:

- = No growth.
 1+ = Very slight growth.
 2+ = Light to moderate growth.
 3+ = Normal heavy growth.

The foregoing tests indicate that an excellent product is produced by the composition containing 0.5% of each of the "active ingredients." All three soaps provided the activity shown in Tables I-A, II-A and III-A at the germicidal level indicated.

EXAMPLE V

Experiments were carried out to determine the variation of synergistic effect with changes in the ratio of the component "active ingredients." All experiments were carried out in a toilet soap medium. For this purpose the individual germicidal compounds or mixtures of compounds were incorporated at a total germicidal level of 1.0% into a conventional toilet soap base, obtained from the saponification of a blend of 20% coconut oil and 80% inedible tallow. This was accomplished by passing a blend of the dry germicidal ingredient and soap chips (moisture content 11%) repeatedly over a three-roll laboratory soap mill until the blend appeared physically homogeneous. The blended soap chips were then dissolved in water to give a 1.0% soap solution, which corresponds to an 0.01% concentration of germicidal agent. Since some of the latter are not very water-soluble, these soap solutions were shaken before each test to insure a uniform suspension in water.

The bacteriological evaluations were carried out with

a modified agar streak method. Aliquots of the 1.0% test soap solutions were added to measured amounts of liquid glucose tryptone extract agar, and the resulting mixture was poured into Petri dishes. As soon as the agar had hardened, its surface was streaked with a standard loop containing a 24-hour culture of *S. aureus* F.D.A. strain No. 209. After an incubation period of 48 hours at 37° C. the plates were examined visually, and the amount of growth was recorded.

In this manner a ratio study of the synergistic pair TCC and hexachlorophene was carried out, the results of which are summarized in Table I. The analogous study of the pair TCC and bithionol was carried out by using the same method, and the results of this study are summarized in Table II. The growth was rated and coded in the following manner: 0=no growth; 1=slight growth, where only a few sporadic colonies can be seen on the plates; 2=moderate growth, where growth occurs along the streaks but one-half or more of the surface of the plate still shows little or no growth; 3=heavy growth, where there is luxuriant growth over practically the entire surface of the plate.

Table I

ANTIBACTERIAL EFFECTIVENESS OF VARIED RATIOS OF HEXACHLOROPHENE AND 3,4,4'-TRICHLOROCARBANILIDE (TCC) IN SOAP (MODIFIED AGAR STREAK METHOD)

Ratio	Bacterial growth ratings—Total antibacterial agent	
	At 0.04 p.p.m.	At 0.02 p.p.m.
100% Hexachlorophene, 0% TCC.....	2	3
90% Hexachlorophene, 10% TCC.....	0	2
70% Hexachlorophene, 30% TCC.....	0	2
50% Hexachlorophene, 50% TCC.....	0	1
40% Hexachlorophene, 60% TCC.....	1	2
30% Hexachlorophene, 70% TCC.....	1	3
20% Hexachlorophene, 80% TCC.....	1	3
10% Hexachlorophene, 90% TCC.....	2	3
0% Hexachlorophene, 100% TCC.....	3	3

Code:

- 0 = No growth.
 1 = Slight growth.
 2 = Moderate growth.
 3 = Heavy growth.

Table II

ANTIBACTERIAL EFFECTIVENESS OF VARIED RATIOS OF BITHIONOL AND 3,4,4'-TRICHLOROCARBANILIDE (TCC IN SOAP (MODIFIED AGAR STREAK METHOD)

Ratio	Bacterial growth ratings—Total antibacterial agent	
	At 0.04 p.p.m.	At 0.02 p.p.m.
100% TCC, 0% Bithionol.....	1	3
90% TCC, 10% Bithionol.....	0	3
70% TCC, 30% Bithionol.....	0	3
60% TCC, 40% Bithionol.....	0	2
50% TCC, 50% Bithionol.....	0	1
40% TCC, 60% Bithionol.....	0	1
30% TCC, 70% Bithionol.....	0	3
20% TCC, 80% Bithionol.....	1	3
10% TCC, 90% Bithionol.....	3	3
0% TCC, 100% Bithionol.....	3	3

Code:

- 0 = No growth.
 1 = Slight growth.
 2 = Moderate growth.
 3 = Heavy growth.

As indicated above, synergistic results were obtained when the ratio of the bisphenols (hexachlorophene or bithionol) to trichlorocarbaniilide was between 90-10 parts by weight of the bisphenol to 10-90 parts by weight of the trichlorocarbaniilide. In other words, the ratio was between 1-9 parts of bisphenol to between 9-1 parts of trichlorocarbaniilide. The preferred range, as already stated, was between 1-7 parts of the bisphenol to 7-1

parts of the trichlorocarbanilide. In a soap containing a germicidal concentration of hexachlorophene or bithionol, we prefer to add trichlorocarbanilide in the proportion of between 1-6 parts to between 7-1 parts of the hexachlorophene or bithionol.

The results hereinabove set out with respect to a specific soap (20 coco and 80 tallow soap) are obtained with soaps generally. For example, any fatty acid soap will produce these results, such as sodium laurate, potassium stearate, sodium oleate, potassium myristate. The synergistic action is independent of the soap vehicles as shown by the activity of the ingredients in non-detergent vehicles and by their activity in anionic detergents other than soap and in non-ionic systems. At the same time, soap is a system in which the synergistic components are highly effective.

While this invention has been described and exemplified in terms of its preferred embodiments, those skilled in the art will appreciate that variations can be made without departing from the spirit and scope of the invention.

We claim:

1. An antiseptic composition containing as its essential active ingredients a synergistic combination of 2,2'-dihydroxy-3,5,6,3',5',6'-hexachlorodiphenyl methane and a polyhalocarbanilide selected from the group consisting of 3,4,4'-trichlorocarbanilide and 3,3',4-trichlorocarbanilide, the proportion of said hexachlorodiphenyl methane to said trichlorocarbanilides being about 9 to 1 parts of the hexachlorodiphenyl methane to about 1 to 9 parts by weight of said trichlorocarbanilides, said composition containing from about 0.2% to about 5.0% by weight of said hexachlorodiphenyl methane and said trichlorocarbanilides.

2. An antiseptic composition comprising soap containing as its essential active ingredients from about 0.2% to about 5.0% by weight of a mixture of 2,2'-dihydroxy-3,5,6,3',5',6'-hexachlorodiphenyl methane and a polyhalocarbanilide selected from the group consisting of 3,4,4'-trichlorocarbanilide and 3,3',4-trichlorocarbanilide, the proportion of said hexachlorodiphenyl methane to said trichlorocarbanilides being about 9 to 1 parts of the hexachlorodiphenyl methane to about 1 to 9 parts by weight of said trichlorocarbanilides.

3. The composition of claim 2 wherein said polyhalocarbanilide is 3,4,4'-trichlorocarbanilide.

4. An antiseptic composition comprising soap and about 1% by weight based upon the soap of a mixture of about equal parts by weight of 2,2'-dihydroxy-3,5,6,3',5',6'-hexachlorodiphenyl methane and a polyhalocarbanilide selected from the group consisting of 3,4,4'-trichlorocarbanilide and 3,3',4-trichlorocarbanilide.

5. The composition of claim 4 wherein said polyhalocarbanilide is 3,4,4'-trichlorocarbanilide.

6. An antiseptic composition comprising soap and about 1½ percent by weight based upon the soap of a mixture of equal parts by weight of 2,2'-dihydroxy-3,5,6,3',5',6'-hexachlorodiphenyl methane and a polyhalocarbanilide selected from the group consisting of 3,4,4'-trichlorocarbanilide and 3,3',4-trichlorocarbanilide.

7. The composition of claim 6 wherein said polyhalocarbanilide is 3,4,4'-trichlorocarbanilide.

8. An antiseptic composition comprising soap containing from about ½ to about 3% by weight of a mixture of about equal parts of 2,2'-dihydroxy-3,5,6,3',5',6'-hexachlorodiphenyl methane and 3,4,4'-trichlorocarbanilide.

9. An antiseptic composition comprising soap and a mixture of 2,2'-dihydroxy-3,5,6,3',5',6'-hexachlorodiphenyl methane and 3,4,4'-trichlorocarbanilide in which the ratio of the said trichlorocarbanilide to 2,2'-dihydroxy-3,5,6,3',5',6'-hexachlorodiphenyl methane is about 9 to 1 parts by weight of said trichlorocarbanilide to about 1 to 9 parts by weight of said 2,2'-dihydroxy-3,5,6,3',5',6'-hexachlorodiphenyl methane, said trichlorocarbanilide and said 2,2'-dihydroxy-3,5,6,3',5',6'-hexachlorodiphenyl methane being present in said soap at a total level of about 1% by weight of said soap.

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