United States Patent

Carroll et al.

[15] **3,671,630**

[45] **June 20, 1972**

[54] HALOGENATED PHENOLIC GERMICIDAL COMPOSITIONS CONTAINING TERPENE COLOR STABILIZERS

[72] Inventors: **Francis Emery Carroll**, Wyckoff; **Walter Charles Seebold**, Westwood, both of N.J.

[73] Assignee: **Lever Brothers Company**, New York, N.Y.

[22] Filed: **Aug. 17, 1970**

[21] Appl. No.: **64,623**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 673,264, Oct. 6, 1967, abandoned.

[52] **U.S. Cl.**.....**424/174,** 252/106, 252/107, 424/195, 424/230, 424/317, 424/347, 424/355, 424/356

[51] **Int. Cl.**.....**A01n 9/30,** C11d 3/48, C11d 9/50

[58] **Field of Search**.....424/174, 195, 59, 60, 230, 424/317, 347, 355, 356; 252/106, 107; 260/489, 652.5

[56] **References Cited**

UNITED STATES PATENTS

2,059,125	10/1936	Lyons	424/174 X
2,267,200	12/1941	Hersberger	425/59
2,867,668	1/1959	Theimer	260/489 X
2,906,711	9/1959	Stecker	252/106
3,075,003	1/1963	Blumenthal	260/489 X
3,085,066	4/1963	Mitoray et al	252/106 X

Primary Examiner—Albert T. Meyers
Assistant Examiner—Leonard Schenkman
Attorney—Brumbaugh, Graves, Donohue & Raymond

[57] **ABSTRACT**

Aqueous solutions containing halogenated phenolic germicidal compositions are stabilized against color change on exposure to light by providing in the solutions an effective amount of a discoloration inhibitor selected from the group consisting of alpha-phellandrene, allo ocimene, ocimene, terpinolene, myrcene, isoprene, rosin, tall oil, myrcene hydrate, and abietic acid. The solutions may also contain up to 35 percent of a detergent and other conventional detergent adjuvants.

22 Claims, No Drawings

HALOGENATED PHENOLIC GERMICIDAL COMPOSITIONS CONTAINING TERPENE COLOR STABILIZERS

This application is a continuation-in-part of application, Ser. No. 673,264, filed Oct. 6, 1967, now abandoned.

The present invention relates to aqueous solutions containing halogenated phenolic germicidal compositions which have improved stability against discoloration by light.

Aqueous solutions containing halogenated phenolic germicidal compositions, such as tribromosalicylanilide (TBS), dibromosalicylanilide (DBS), and hexachlorophene, change color on exposure to sunlight, actinic light and even artificial light for prolonged periods of time. The freshly made aqueous compositions are colorless or slightly yellowish, but change to a dark amber within a very few hours of exposure to light. Special precautions are thus necessary in the manufacture, packaging and distribution of these germicidal solutions to insure that they do not become exposed to light and undergo undesirable color change.

One prior art attempt to improve the color stability of germicidal compositions is by the incorporation therein of an inorganic sulfite. While such compositions have improved stability against discoloration, the inorganic sulfite imparts an undesirable sour odor which consumers dislike. More importantly, where these germicidal liquid compositions containing sulfite are packaged and sold in resilient containers, it has been noted that the containers are subject to significant collapse or paneling of their resilient walls. This is thought to be occasioned by the removal of oxygen from the head space of the resilient container due to the presence of the inorganic sulfite reducing agent.

It is accordingly an object of the present invention to provide an aqueous germicidal composition based on halogenated phenolic germicides, which solutions have improved stability to discoloration by light and which, at the same time, are free of the disadvantages of the prior art set forth above. It is a further object to provide aqueous germicidal detergent compositions having the same advantages.

It has now been found that aqueous solutions of halogenated phenolic germicides can be significantly stabilized against color change in the presence of light by incorporating in such compositions, as stabilizers, a compound selected from the group consisting of alpha-phellandrene, allo ocimene, ocimene, terpinolene, myrcene, isoprene, rosin, tall oil, myrcene hydrate and abietic acid. Of these materials, the most effective are alpha-phellandrene, allo ocimene, ocimene, terpinolene and myrcene. The isoprene and abietic acid are somewhat less effective but, nevertheless, retard color development to a significant extent.

These compositions are terpenes and are generally representative of many of the classes of known terpenes. For example, the ocimene and myrcene are acyclic monoterpenoids. The terpinolene and the alpha-phellandrene are cyclic monoterpenoids. Abietic acid is a diterpenoid.

In addition to the pure terpenes, equivalent and satisfactory results have been obtained with certain mixtures derived from natural sources which contain significant quantities of those materials defined above. For example, a composition available as Rosin WW contains significant quantities of abietic acid and provides results similar to those obtained with abietic acid itself. An analysis of a typical wood rosin is as follows:

Fraction	%
Neutral	10
Two-double-bond abietic-type acids	53
Dihydro acids (abietic acid pimaric-type)	13
Tetrahydro acids (includes pimaric-type acids)	16
Dehydroabietic acid	2
Bicarbonate-soluble (oxidized acids)	6

Sinpine, a commercially available mixture of terpenes, provides excellent results. The approximate composition of Sinpine is as follows:

Terpinolene	10%
α pinene	15%
α terpinene	20%
Dipentene	20%
Cineol	10%
Camphene	15%
γ terpinene	5%
Unidentified	5%
Total:	100%

Mugol and Myrcenol are trade names for mixtures of terpene alcohols which have been found to provide stabilizing activity equivalent to that obtained with isoprene and abietic acid. The structure of Myrcenol is given in U.S. Pat. No. 3,075,003; it is called myrcene hydrate in line 43, column 2. Mugol is the compound shown in U.S. Pat. No. 2,867,688, top of column 3, as a mixture of 3 isomers: viz., cis and trans at the indicated double bond in the structure in line **15**, the other double bond being trans, and in the structure in line **19** the double bond being trans. The mixture consists of about 50 percent of the cis-trans mixture in ratio of 1:2 and the balance being the structure in line 19.

Tall oil, a distilled product containing a high percentage of rosin acids also provides results approximating those obtained by abietic acid. Tall oil has the following analysis:

Fraction	%
Fatty acids mainly of the oleic series	25–60
Resin acids, which may include 50 to 90% abietic acid	25–60
Unsaponifiable material which may contain phytosterols, lignins, mercaptans and higher alcohols	7–20

On the other hand, many terpenes and related compounds have been found to be completely ineffective. The following compounds gave no color stabilizing effect: linalyl acetate, geranyl acetate, limonene, alpha pinene, beta pinene, terpinyl acetate, neryl acetate, alpha-terpineol, quinone, methyl eugenol, camphene, amyl cinnamic aldehyde, laevo carvone, pipertone, colchicine, beta ionone and menthanyl acetate terpenes.

The aqueous germicidal solutions of the present invention usually contain a solubilizer. The brominated salicylanilides are highly insoluble in water. The potassium salt of tribromosalicylanilide is slightly soluble in water at room temperature. A solvent for the germicides is required which is also miscible in water. Water admixed with a lower aliphatic monohydric or polyhydric alcohol, such as methanol, ethanol, propanol or glycol is useful. Solvents of this nature also include acetone, xylene sulfonate and n-propyl alcohol. In compositions containing mixed detergent active materials, the germicides may be dissolved in one of these materials. For example, in compositions containing lauric diethanolamide as a suds booster, the germicide can be dissolved in the amide prior to formulating the balance of the composition.

The halogenated phenolic germicides used to make the color stabilized compositions of this invention should be present in germicidal effective amounts. The appropriate amount will vary, depending upon the nature of the solution, and generally will range from 0.1 percent to about 4 percent by weight. A preferred amount is about 0.4 percent by weight of the total composition.

The halogenated phenolic germicides are well known conventional materials, representative examples of which include the normal and alkali metal salt forms of 4'-monobromosalicylanilide, 5-monobromosalicylanilide, 4',5-dibromosalicylanilide, 3,5-dibromosalicylanilide, 3,4',5-tribromosalicylanilide, 3,4',5-trichlorosalicylanilide, 3',4',5-trichlorosal-

icylanilide, 3,3',4',5-tetrachlorosalicylanilide, trichlorocarbanilide, and hexachlorophene or 2,2'-dihydroxy, 3,5,6,3',5',6'-hexachlorodiphenyl methane. Of these the preferred halogenated phenolic germicides are hexachlorophene and the normal and equivalent alkali metal salt forms of 3,4',5-tribromosalicylanilide and 4',5-dibromosalicylanilide as well as mixtures thereof containing at least about 50 percent by weight of 3,4',5-tribromosalicylanilide. Other halogenated phenolic germicides which discolor on exposure to light and which may be stabilized by the addition of terpene compositions according to this invention include 2,4,6-trichlorophenol, tetrachlorophenol, 4-chloro-2-cyclopentylphenol, sodium pentachlorophenate, p-chloro-m-cresol, bithionol or 2,2'-thiobis (4,6-dichlorophenol), 3-[2-hydroxy-3,5-dichlorophenyl]-5,7-dichlorocoumaran, o-benzyl-p-chlorophenol and 4,6-dibromocresol.

In accordance with one preferred embodiment of the invention, the aqueous halogenated germicide solution contains a detergent. Ammonium alkyl aryl sulfonate is an example of a suitable detergent and may be used alone or in combination with an ammonium C_{14}–C_{12} alcohol 3EO sulfate and lauric diethanolamide. Other compatible detergents generally known in the art may be employed. Typical of such detergents are anionic, cationic or nonionic non-soap detergents and water-soluble fatty acid soaps. Furthermore, other detergent adjuvants, such as inorganic detergents, inorganic builder salts, sequestering agents, hydrotropes, opacifiers, perfumes, soil suspending agents, optical brighteners, colorants, and abrasive particles may be used. Such materials are conventional materials for the formulation of aqueous detergent compositions and have been fully described in the technical and patent literature, for example, in "Soaps and Detergents" by Thomssen and McCutcheon and "Encyclopedia of Chemical Technology" by Kirk and Othmer.

The stabilizers of this invention are used in an amount sufficient to retard or prevent discoloration of the aqueous germicidal compositions. Generally speaking, amounts ranging from 0.25 to 1 percent have been effective with germicide levels of 0.4 percent. In addition, stabilizer levels ranging from 1 to 5 percent have been useful with a 4 percent level of germicide. Reverting to specific examples, an aqueous solution containing TBS as the germicide at a level of 0.4 percent is completely stabilized for 72 hours exposure to light by the use of alpha-phellandrene at a level ranging from 0.25 to 1 percent.

With an aqueous solution containing 0.4 percent TBS, a level of myrcene ranging from 0.5 to 1 percent was an effective stabilizer, while with the same TBS solution, ocimene was effective over a range of 0.25 to 1 percent, and abietic acid was partially effective over a range of 0.1 to 0.5 percent.

The following examples serve to illustrate the invention previously disclosed and are not intended to limit it in any way. All percentages are by weight unless otherwise indicated.

EXAMPLE I

Aqueous germicidal compositions were prepared to contain 0.4 percent of tribromosalicylanilide and 1 percent of each of a series of organic compounds as color stabilizers. The liquids were prepared by dissolving the TBS in acetone and water and by thereafter adjusting the pH of the liquid to the 6–7 range with sodium hydroxide. The composition of the liquid was a follows:

Ingredients	% by Weight
TBS	0.4
Acetone	93.6
Water + misc.	5.0
Stabilizer	1.0
Total:	100.0

After preparation, samples of the various liquids containing the various color stabilizers were stored in glass bottles on a roof so as to provide constant exposure to light during the daytime hours. The color of the liquids was graded at the time the liquids were made and at various intervals thereafter. The following legend was used to evaluate the compositions in conducting the visual color grading tests:

0 — Colorless to slight yellow tint
1 — Very slightly yellow
2 — Slightly yellow to slightly amber
3 — Yellow to medium amber
4 — Amber

Table 1 below gives the values assigned to the compound initially and after 2 hours, 15 hours, and 106 hours of exposure to daylight. Liquids having a color grading of 3 or more are considered unsatisfactory with respect to color stability.

TABLE I

Stabilizer	Visual Color Gradings of Liquids After Exposure to Daylight for 0 Hrs.	2 Hrs.	15 Hrs.	106 Hrs.
Terpinolene	0	1	2	1
Alpha-phellandrene	0	0	0	0
Allo ocimene	0	0	0	0
Sinpine*	0	1–2	3	1–2
Sinpine (redistilled)	0	1–2	2	1
Ocimene	0	0	0	0
Myrcene	0	0	2	1–2
*Sinpine is a mixture of terpenes supplied by Givaudan-Delawanna Inc.				
Abietic acid	1	1–2	2	2
Rosin WW**	0	1–2	2	1–2
None	0	2	4	4

**About 90% rosin acids and 10% nonacids.

As will be seen from Table 1, the control liquid on exposure to light turns slightly yellow in 2 hours and amber in 15 hours. The liquids containing alpha-phellandrene, allo ocimene, and terpinolene had not undergone appreciable color change after exposure to light for 106 hours. The liquids containing Sinpine, myrcene, abietic acid and Rosin WW developed only a slightly yellow color after these periods of time and therefore could be considered as having a significant retarding effect in these instances.

EXAMPLE II

A liquid composition was prepared according to the invention to contain 0.4 percent TBS in acetone and water with no adjustment of the pH taking place after the addition of the color stabilizers. These liquids had a pH within the range of 3–3.5. Their composition was as follows:

Ingredients	% by Weight
TBS	0.4
Acetone	79.6
Stabilizer	1.0
Water and Misc.	19.0
Total:	100.0

The effect of light on the color of the above liquid containing various stabilizers is given in Table 2 below. After 72 hours, the initially colorless liquids without stabilizers had changed to a yellow color. The other compounds prevented a color change.

TABLE 2

Stabilizer	Visual Color Gradings of Liquids After Exposure to Light for 0 Hrs.	72 Hrs.

Abietic acid	0	0
Rosin WW*	0	0
Myrcene	0	0
Ocimene	0	0
Alpha-phellandrene	0	0
Allo ocimene	0	0
Mugol**	0	0
Sinpine	0	
None	0	3

*Described in Example I

**A terpene alcohol, supplied by International Flavors and Fragrances, Inc.

EXAMPLE III

Aqueous germicidal compositions were prepared containing 0.4 percent TBS in alcohol and water and adjusted to a pH of 10.3 with potassium hydroxide. The composition of the germicidal liquid was as follows:

Ingredients	% by Weight
TBS	0.4
N-propyl alcohol	50.0
KOH (50%)	0.125
Stabilizer	1.0
Water and misc.	48.475
Total:	100.000

Table 3 below gives the visual color gradings made when the solutions were initially prepared, and after 72 hours of exposure to light.

TABLE 3

Stabilizer	Visual Color Gradings of Liquids After Exposure to Light for 0 Hrs.	72 Hrs.
Abietic acid	0	0
Rosin WW	0	0
Allo ocimene	0	0
Sinpine	0	0
Pipertone	0	4
None	0	4

Legend
0 – colorless to slight yellow tint
4 – amber

The control liquid containing no stabilizer and the liquid containing pipertone were amber. The remaining liquids ranged from colorless to a slight yellow tint.

EXAMPLE IV

Germicidal liquid formulations containing 4 percent TBS and various levels of alpha-phellandrene were tested for light stability. The composition of the liquids were as follows:

Ingredients	% by Weight
TBS	4.0
Acetone	86–91
Stabilizer	0–5
Water	5.0

The compositions had a pH within the range of 2.3–2.7.

Table 4 gives the visual color gradings obtained. A reading of 0 indicates a colorless liquid, whereas a reading of 3 designates a yellow to medium amber liquid.

TABLE 4

Stabilizer	Visual Color Gradings of Liquids After Exposure to Daylight for 0 Hrs.	132 Hrs.
1% alpha-phellandrene	0	0
3% alpha-phellandrene	0	0
5% alpha-phellandrene	0	0
None	0	3

EXAMPLE V

A germicidal liquid formulation containing 1 percent TBS and 1 percent of various color stabilizers was tested for light stability. The composition of the liquid was as follows:

Ingredients	% by Weight
TBS	1.0
Acetone	93.0
Water	5.0
Stabilizer	1.0
Total:	100.0
Ph 6.6	

Table 5 below shows the results of the tests. In the visual color gradings, 0 is colorless, 2 is slightly yellow to slightly amber, and 4 is amber.

TABLE 5

Stabilizer	Visual Color Gradings of Liquids After Exposure to Daylight for 0 Hrs.	106 Hrs.
Allo ocimene	0	2
Alpha-phellandrene	0	2
None	0	4

The above demonstrates that a germicidal liquid containing 1 percent TBS changes from a colorless liquid to an amber liquid when exposed to daylight. The color began to develop almost immediately on exposure to light and the liquid was noticeably colored in about 2 hours. Liquids containing the stabilizers were stabilized as a slight yellow liquid as compared to the amber or reddish brown color with the control liquid.

EXAMPLE VI

Germicidal liquids containing hexachlorophene, both with and without color stabilizers, were tested for light stability. The composition of the germicidal liquids was as follows:

Ingredients	% by Weight
Hexachlorophene	0.4
Acetone	54.0
Water	44.6
Stabilizer	1.0
Total	100.0

Table 6 below gives the visual color gradings obtained by using various stabilizers in the above germicidal liquid compositions. In the gradings, 0 indicates a colorless solution, 3 a yellow to medium amber and 4 designates amber.

TABLE 6

Stabilizer	Visual Color Gradings of Liquids After Exposure to Daylight for 0 Hrs.	336 Hrs.
Alpha-phellandrene	0	0
Allo ocimene	0	0
Benzene	0	4
Laevo carvone	0	3
None	0	4

The liquids containing hexachlorophene changed from colorless to amber on exposure to light. Alpha-phellandrene and allo ocimene prevented discoloration of the liquid. Benzene and laevo carvone were ineffective as color stabilizers.

EXAMPLE VII

Germicidal liquid detergent formulations containing 0.4 percent hexachlorophene and 10 percent dodecylbenzene sulfonate, together with various color stabilizers were prepared. The compositions had the following formula, with a pH of 6–7.5:

Ingredients	% by Weight
NH_4 Ucane 12 sulfonate	10.0
Hexachlorophene	0.4
Acetone	46.0
Water	42.6
Stabilizer	1.0
Total:	100.0

Color gradings of the solutions were made on the following basis: 0 = colorless to a slightly yellow tint; 1 = slightly yellow, and 4 = amber.

Table 7 below summarizes the results obtained.

TABLE 7

Stabilizer	Visual Color Gradings of Liquids After Exposure to Daylight for 0 Hrs.	336 Hrs.
Alpha-phellandrene	0–1	0
Allo ocimene	0–1	0
Benzene	0–1	4
Laevo carvone	0–1	4
None	0–1	4

The detergent formulations containing hexachlorophene changed from a colorless liquid to an amber liquid on exposure to daylight. Alpha-phellandrene and allo ocimene preserved the color of the liquid, whereas benzene and laevo carvone had no stabilizing effect.

EXAMPLE VIII

A germicidal liquid detergent containing TBS was prepared having the following ingredients in the indicated amounts:

Ingredients	% by Weight
Nh_4 C_{14}–C_{12} alcohol 3EO sulfate	10.0
TBS	0.4
Acetone	50.6
Stabilizer	1.0
Water and misc.	38.0
Total:	100.0

The liquids were prepared by dissolving the detergent and TBS in acetone and water. The color stabilizer was added last and the pH of the liquid was adjusted to within the range of 6–7.5 with either sodium or ammonium hydroxide or sulfuric acid. The acetone was used to dissolve the TBS which is insoluble in water. Samples of the liquid containing various organic components undergoing evaluation as stabilizers were stored on a roof in glass bottles for exposure to light.

Table 8 below gives the visual color gradings for these substances after various periods of exposure to daylight. 0 is colorless to a slightly yellow tinted solution. 1 indicates very slightly yellow. 2 indicates slightly yellow to slightly amber, and 3 is yellow to medium amber.

TABLE 8

Stabilizer	Visual Color Gradings of Liquids After Exposure to Daylight for 0 Hrs.	2 Hrs.	35 Hrs.	336 Hrs.
Linalyl acetate	0	2	3	2
Terpinyl	0	2	2	2
Neryl acetate	0	2	3	2
Terpinolene	0	2	2	0
Beta pinene	0	2	2	2
Beta ionone	0	2	3	2
Methyl eugenol	0		2	2
Mugol	0	2	2	0
Myrcenol	0		2	1
Methanyl acetate terpenes	0	2	2	2
Alpha-phellandrene	0	0	0	0
Allo ocimene	0	0	0	0
Sinpine	0	0	1	0
Sinpine (redistilled)	0	0	0	0
Ocimene	0	0	0	0
Myrcene	0	0	1	0
Abietic acid	1	2	1	2
Rosin WW	0	0	0	0
Tall oil fatty acid	0	2	2	2
Isomerized linoleic acid	0	2	1	2
None	0	2	3	3

The liquid detergent containing no additive changed from a colorless liquid to a yellow or slightly amber liquid in 2 hours and to a yellow to medium amber liquid in 35 hours. The liquids containing terpinolene, Mugol, alpha-phellandrene, allo ocimene, Sinpine, ocimene, myrcene and Rosin WW were graded 0 after 336 hours of exposure to light.

EXAMPLE IX

Germicidal aqueous detergent compositions were prepared containing 0.4 percent TBS, 10 percent ammonium dodecylbenzene sulfonate and 1 percent of various organic compounds as color stabilizers. After storing these solutions for a period of time, they were graded according to the following visual evaluations:

0 — colorless to slightly yellow tint
1 — very slightly yellow
2 — slightly yellow to slightly amber
3 — yellow to medium amber
4 — amber

Table 9 below summarizes the results obtained:

TABLE 9

Stabilizer	Visual Color Gradings of Liquids After Exposure to Daylight for 0 Hrs.	2 Hrs.	42 Hrs.	280 Hrs.
Terpinolene	0	2	2	2
Beta pinene	0	2	2	2

Mugol	0	2	1–2	2
Myrcenol	0	2	1–2	2
Alpha-phellandrene	0	0	0	0
Allo ocimene	0	0	0	0
Sinpine	0	2	1–2	1
Ocimene	0	2	1–2	1
Myrcene	0	2	0	1
Abietic acid	1	2	2	2
Rosin WW	0	1	1–2	1
None	0	2	3	4

The data show that the liquid containing no stabilizer changed from a colorless liquid to one having a slight yellow to a slight amber tint in 2 hours, and to an amber liquid after 280 hours exposure to light. The liquids containing alpha-phellandrene and allo ocimene were colorless liquids after 280 hours of exposure to light. The other stabilizers were effective but to a lesser extent.

EXAMPLE X

Germicidal liquid detergents containing 0.4 percent TBS, 10 percent lauric diethanolamide and 1 percent of various organic compounds as color inhibitors were prepared and were visually evaluated according to the following table:

0 — Colorless to light yellow tint
1 — very slightly yellow
2 — slightly yellow to slightly amber
3 — yellow to medium amber

Table 10 below gives the results of these experiments.

TABLE 10

Additive	Visual Color Gradings of Liquids After Exposure to Daylight for 0 Hrs.	2 Hrs.	35 Hrs.	336 Hrs.
Terpinolene	0	2	2	0
Beta pinene	0	2	2	1
Mugol	0	2	3	1
Myrcenol	0	2	2	1
Alpha-phellandrene	0	0	0	0
Allo ocimene	0	0	0	0
Sinpine	0	2	2	0
Sinpine (redistilled)	0	2	0	0
Ocimene	0	0	0	0
Myrcene	0	2	0	0
Abietic acid	1	2	2	1
Rosin WW	0	2	2	1
Tall oil fatty acid	0	3	2	1
None	0	3	3	3

The liquids containing terpinolene, alpha-phellandrene, allo ocimene, sinpine, ocimene, and myrcene were colorless liquids after 336 hours of exposure to light, whereas the control changed to a yellow to a medium amber liquid after 2 hours.

EXAMPLE XI

A germicidal liquid detergent composition was prepared to have the following formula:

Ingredients	% by Weight
NH_4 dodecylbenzene sulfonate (Ucane 12)	17.0
NH_4 Alfol 1412 3EO sulfate	12.0
Lauric diethanolamide	6.0
NH_4 xylene sulfonate	9.0
TABS	0.4
Water and misc.	54.6
Stabilizer	1.0
Total:	100.0

The liquids were prepared by dissolving the TBS in lauric diethanolamide and then adding this mixture to an aqueous solution of the two sulfonates and the sulfate. The color stabilizer was then added and the pH of the material adjusted to 6–7 by the addition of sulfuric acid. The liquids were stored for varying periods of time and then evaluated according to the following:

0 — colorless to slightly yellow tint
1 — very slightly yellow to very slightly amber
2 — slightly yellow to slightly amber
3 — yellow to medium amber
4 — amber
5 — dark amber

Table 11 below gives the results of these experiments.

TABLE 11

Stabilizer	Visual Color Gradings of Liquids After Exposure to Daylight for 0 Hrs.	2 Hrs.	30 Hrs.	60 Hrs.	194 Hrs.
Allo ocimene	1	1	1	1	1
Alpha-phellandrene	1	1	1–2	2	1–2
Mugol	1	2	2		2
Myrcenol	1	2	3		3
Sinpine	1	2	2		2
Sinpine (redistilled)	1	1	2	–	1–2
Terpinolene	1	1	1–2	–	1–2
Ocimene	1	1	1–2	2	1–2
None	1	3	5		5
Myrcene	1	–	–	2	–

The control liquid containing no additive changed to a medium amber color in 2 hours and to a dark amber after 30 hours of exposure to light. The liquids containing allo ocimene, redistilled Sinpine, terpinolene and ocimene maintained a very slight yellow to a slight amber color after 194 hours of exposure to light.

EXAMPLE XII

A number of germicidal liquid detergents having the composition given in Example XI were prepared containing 0.4 percent TBS and varying levels of alpha-phellandrene. Table 12 below summarizes the results of the visual color evaluations of this series of tests, using the grading system of Example XI.

TABLE 12

% Alpha-phellandrene	Visual Color Grade of Liquids Exposed to Light for 0 Hrs.	72 Hrs.
0	1	5
0.1	1	3
0.25	1	1
0.5	1	1
1.0	1	1

EXAMPLE XIII

The effect of varying the levels of myrcene in the composition of Example XI is given in the following table. The visual color grading system of Example XI was used.

TABLE 13

% Myrcene	Visual Color Grade of Liquids Exposed to Light for 0 Hrs.	72 Hrs.
0	1	5
0.1	1	5
0.25	1	5

0.5	1	1
1.0	1	1

EXAMPLE XIV

The effect of varying the ocimene levels in the germicidal composition of Example XI is given in the following table. The visual color grading system of Example XI was used.

TABLE 14

% Ocimene	Visual Color Grade of Liquids Exposed to Light for 0 Hrs.	72 Hrs.
0	1	5
0.1	1	3
1 0.25	1	1
0.5	1	1
1.0	1	1

EXAMPLE XV

The effect of varying the Rosin WW levels in the germicidal composition of Example XI is given in the following table. The visual color grading system of EXample XI was used.

TABLE 15

% Rosin WW	Visual Color Grade of Liquids Exposed to Light for 0 Hrs.	72 Hrs.
0	1	5
0.1	1	5
0.15	1	5
0.20	1	1–2
0.25	1	1–2
0.5	1	1–2
1.0	1	1–2

EXAMPLE XVI

The effect of varying the abietic acid levels in the germicidal composition of Example XI is given in the following table. The visual color grading system of Example XI was used.

TABLE 16

% Abietic Acid	Visual Color Grade of Liquids Exposed to Light for 0 Hrs.	72 Hrs.
0	1	5
0.05	1	5
0.1	1	3
0.25	1	1–2
0.5	1	1–2

EXAMPLE XVII

Two germicidal solutions containing 1.0 percent 2,4,6-trichlorophenol and 75 percent ethanol were prepared. The first solution, A, simply contained a balance of water while the second solution, A′, contained in addition 1.0 percent allo ocimene. The two solutions were visually color graded after exposure to light according to the following legend:

0 — colorless
1 — light pinkish violet
2 — medium pinkish violet
3 — medium reddish violet
4 — dark reddish violet
5 — very dark reddish violet

The results of this experiment are reported below in Table 17:

TABLE 17

Hours	Visual Color Grading After Exposure to Light for Germicidal Composition A	A′
0	0	0
36	1	0
60	2	0
84	3	0
120	4	0
144	4	0
168	4	0
204	5	0

EXAMPLE XVIII

Two germicidal solutions containing 1 percent tetrachlorophenol and 75 percent ethanol were prepared. The first solution, B, simply contained a balance of water while the second solution, B′, contained in addition 1.0 percent allo ocimene. The two solutions were visually color graded after exposure to light according to the following legend:

0 — colorless
1 — very light violet
2 — light violet
3 — medium violet
4 — dark violet
5 — very dark violet

The results of this experiment are reported below in Table 18:

TABLE 18

Hours	Visual Color Grading After Exposure to Light for Germicidal Composition B	B′
0	0	0
36	1	0
60	2	0
84	2	0
120	3	0
144	4	0
168	5	0
204	5	0

EXAMPLE XIX

Two germicidal solutions containing 1.0 percent 4-chloro-2-cyclopentylphenol and 75 percent ethanol were prepared. The first solution, C, simply contained a balance of water while the second solution, C′, contained in addition 1.0 percent allo ocimene. The two solutions were visually color graded after exposure to light according to the following legend:

0 — trace yellow
1 — slight yellow
2 — light amber

Table 19 gives the results of this experiment:

TABLE 19

Hours	Visual Color Grading After Exposure to Light for Germicidal Composition C	C′
0	0	0
36	0	0
60	1	1
84	1	0
120	1	0
149	1	0
168	2	0

204	2	0

EXAMPLE XX

Two germicidal solutions containing 1.0 percent sodium pentachlorophenate and 75 percent ethanol were prepared. The first solution, D, simply contained a balance of water while the second solution, D', contained in addition 1 percent allo ocimene. The two solutions were visually color graded after exposure to light according to the following legend:

0 — slight yellow
1 — medium brown
2 — dark brown
3 — very dark brown
4 — very dark reddish brown

The results of this experiment are reported in Table 20:

TABLE 20

Visual Color Grading After Exposure to Light for Hours	Germicidal Composition D	D'
0	0	0
36	1	0
60	2	0
84	3	0
120	3	0
144	3	0
168	3	0
0 204	4	0

EXAMPLE XXI

Two germicidal solutions containing 1.0 percent p-chloro-m-cresol and 75 percent ethanol were prepared. The first solution, E, simply contained a balance of water while the second solution, E', contained in addition 1.0 percent allo ocimene. The two solutions were visually color graded after exposure to light according to the following legend:

0 — colorless
1 — slightly pink
2 — medium pink

The results of this experiment are reported in Table 21:

TABLE 21

Visual Color Grading After Exposure to Light for Hours	Germicidal Composition E	E'
0	0	0
36	1	0
60	2	0
84	2	0
120	2	0
144	2	0
168	2	0
204	2	0

EXAMPLE XXII

Two germicidal solutions containing 1.0 percent 2,2'-thiobis(4,6-dichlorophenol) and 75 percent ethanol were prepared. The first solution, F, simply contained a balance of water while the second solution, F', contained in addition 1 percent allo ocimene. The two solutions were visually colored graded after exposure to light according to the following legend:

0 — colorless
1 — medium yellow
2 — medium amber
3 — reddish amber
4 — medium reddish amber
5 — dark amber

The results of this experiment are reported in Table 22:

TABLE 22

Visual Color Grading After Exposure to Light for Hours	Germicidal Composition F	F'
0	0	0
36	1	0
60	2	0
84	2	0
120	3	0
144	4	0
168	4	0
204	5	0

EXAMPLE XXIII

Two germicidal solutions containing 1.0 percent 3',4',5-trichlorosalicylanilide, 10 percent lauric diethanolamide and 75 percent ethanol were prepared. The first solution, G, simply contained a balance of water while the second solution, G', contained in addition 1 percent allo ocimene. The two solutions were visually color graded after exposure to light according to the following legend:

0 — colorless
1 — dark yellow
2 — dark amber
3 — very dark amber
4 — dark reddish - orange
5 — very dark orange

The results of this experiment are reported in Table 23:

TABLE 23

Visual Color Grading After Exposure to Light for Hours	Germicidal Composition G	G'
0	0	0
36	1	0
60	2	0
84	3	0
120	4	0
144	4	0
168	4	0
204	5	0

EXAMPLE XXIV

Two germicidal solutions containing 1.0 percent 3-[2-hydroxy-3,5-dichlorophenyl]-5,7-dichlorocoumaran and 75 percent ethanol were prepared. The first solution, H, simply contained a balance of water while the second solution, H', contained in addition 1.0 percent allo ocimene. The two solutions were visually color graded after exposure to light according to the following legend:

0 — slight lemon yellow
1 — medium amber
2 — brownish amber
3 — medium brown
4 — medium greenish brown

The results of this experiment are reported in Table 24:

TABLE 24

Visual Color Grading After Exposure to Light For Hours	Germicidal Composition H	H'
0	0	0

36	1	0
60	1	0
84	2	0
120	2	0
144	3	0
168	4	0
204	4	0

EXAMPLE XXV

Two germicidal solutions containing 1.0 **percent o-benzyl-p-chlorophenol and** 75 percent ethanol were prepared. The first solution, I, simply contained a balance of water while the second solution, I', contained in addition 1.0 percent allo ocimene. The two solutions were visually color graded after exposure to light according to the following legend:

0 — colorless
1 — very light pink
2 — dark pink
3 — orange - pink
4 — medium orange - pink
5 — light amber
6 — medium amber

Table 25 gives the results of this experiment:

TABLE 25

Visual Color Grading After Exposure to Light for Hours	Germicidal Composition I	I'
0	0	0
36	1	0
60	2	0
84	3	0
120	4	0
144	5	0
168	6	0
204	6	0

EXAMPLE XXVI

Two germicidal solutions containing 1.0 percent 4,6-dibromocresol and 75 percent ethanol were prepared. The first solution, J, simply contained a balance of water while the second solution, J', contained in addition 1 percent allo ocimene. Two solutions were visually color graded after exposure to light according to the following legend:

0 — colorless
1 — medium pink
2 — medium red
3 — medium orange - red
4 — medium orange

Table 26 shows the results of this experiment:

TABLE 26

Visual Color Grading After Exposure to Light for Hours	Germicidal Composition J	J'
0	0	0
36	1	1
60	2	0
84	3	0
120	3	0
144	3	0
168	4	0
204	4	0

EXAMPLE XXVII

Four germicidal solutions having the following compositions were prepared:

Germicidal Composition:	M%	M'%	M''%	M'''%
2,4,6-trichlorophenol	5.0	5.0	5.0	5.0
Ethanol	75.0	75.0	75.0	75.0
Allo ocimene	–	1.0	3.0	5.0
Water	20.0	19.0	17.0	15.0

These solutions were visually color graded at varying time intervals during a 228 hour light exposure period according to the following legend:

0 — colorless
1 — slightly yellow
2 — light reddish purple
3 — dark reddish purple
4 — medium pinkish red
5 — medium crimson
6 — very dark crimson

The results of this experiment are reported in Table 27:

TABLE 27

Visual Color Grading After Exposure to Light for Hours	Germicidal Composition M	M'	M''	M'''
0	0	0	0	0
36	2	0	0	0
84	3	0	0	0
144	4	1	1	0
168	5	1	1	0
192	5	1	1	0
228	6	1	1	0

EXAMPLE XXVIII

Four germicidal solutions having the following compositions were prepared:

Germicidal Composition:	N%	N'%	N''%	N'''%
2,4,6-trichlorophenol	1.0	1.0	1.0	1.0
Ethanol	75.0	75.0	75.0	75.0
Allo ocimene	–	0.10	0.25	0.50
Water	24.0	23.9	23.75	23.50

These solutions were visually color graded at varying time intervals during a 228 hour light exposure period according to the following legend:

0 — colorless
1 — very light pinkish violet
2 — medium reddish violet
3 — light reddish violet
4 — dark reddish violet
5 — very dark reddish violet

The results of this experiment are reported in Table 28:

TABLE 28

Visual Color Grading After Exposure to Light for Hours	Germicidal Composition N	N'	N''	N'''
0	1	1	1	1
24	1	1	1	1
48	2	1	1	1
84	3	1	1	1
108	4	1	1	1
168	4	1	0	0
204	5	2	0	0
228	5	2	0	0

We claim:

1. An aqueous germicidal composition having improved stability against discoloration by light which comprises an aqueous solution containing from about 0.1 percent to about 4 percent by weight of a halogenated phenolic germicide susceptible to discoloration by light, and a discoloration retarding amount of a discoloration inhibitor selected from the group consisting of alpha-phellandrene, allo ocimene, ocimene, terpinolene, myrcene, myrcene hydrate, rosin, tall oil, isoprene and abietic acid.

2. An aqueous germicidal composition having improved stability against discoloration by light which comprises an aqueous solution containing from about 0.1 percent to about 4 percent by weight of a halogenated phenolic germicide selected from the group consisting of 3,4',5-tribromosalicylanilide, 4,5-dibromosalicylanilide, and hexachlorophene, and a discoloration retarding amount of a discoloration inhibitor selected from the group consisting of alpha-phellandrene, allo acimene, ocimene, terpinolene, myrcene, myrcene hydrate, rosin, tall oil, isoprene and abietic acid.

3. The composition according to claim 1 wherein the discoloration inhibitor is selected from the group consisting of alpha-phellandrene, allo ocimene, ocimene, terpinolene, and myrcene.

4. The composition according to claim 1 wherein the inhibitor is present at a level of at least about 0.25 percent by weight.

5. The composition according to claim 1 wherein a solubilizer is also present, said solubilizer being miscible in water and also a solvent for the germicide.

6. The composition according to claim 1 which additionally contains from 1 to 35 percent of a detergent.

7. The composition according to claim 1 wherein the halogenated phenolic germicide is selected from the group consisting of tetrachlorophenol, 4-chloro-2-cyclopentylphenol, sodium pentachlorophenate, p-chloro-m-cresol, 2,2'-thiobis(4,6-dichlorophenol), 3',4',5-trichlorosalicylanilide, 3-[2-hydroxy-3,5-dichlorophenyl]-5,7-dichlorocoumaran, o-benzyl-p-chlorophenol, 4,6-dibromocresol, and 2,4,6-trichlorophenol.

8. The composition according to claim 7 wherein the inhibitor is 1 percent allo ocimene and the germicide is 1 percent tetrachlorophenol.

9. The composition according to claim 7 wherein the inhibitor is 1 percent allo ocimene and the germicide is 1 percent 4-chloro-2-cyclopentylphenol.

10. The composition according to claim 7 wherein the inhibitor is 1 percent allo ocimene and the germicide is 1 percent sodium pentachlorophenate.

11. The composition according to claim 7 wherein the inhibitor is 1 percent allo ocimene and the germicide is 1 percent p-chloro-m-cresol.

12. The composition according to claim 7 wherein the inhibitor is 1 percent allo ocimene and the germicide is 1 percent 2,2'-thiobis(4,6-dichlorophenol).

13. The composition according to claim 7 wherein the inhibitor is 1 percent allo ocimene and the germicide is 1 percent 3-[2-hydroxy-3,5-dichlorophenyl]-5,7-dichlorocoumaran.

14. The composition according to claim 7 wherein the inhibitor is 1 percent allo ocimene and the germicide is 1 percent o-benzyl-p-chlorophenol.

15. The composition according to claim 7 wherein the inhibitor is 1 percent allo ocimene and the germicide is 1 percent 4,6-dibromocresol.

16. The composition according to claim 7 wherein the inhibitor is 1 percent allo ocimene and the germicide is 0.10 to 5 percent 2,4,6-trichlorophenol.

17. An aqueous germicidal composition having improved stability against discoloration by light which comprises from about 0.1 percent to about 4 percent by weight of a halogenated phenolic germicide susceptible to discoloration by light, water, a solubilizer which is miscible in water and is also a solvent for the germicide, from about 1 percent to about 35 percent of detergent, and a discoloration retarding amount of a discoloration inhibitor selected from the group consisting of alpha-phellandrene, allo ocimene, ocimene, terpinolene, myrcene, myrcene hydrate, tall oil, isoprene and abietic acid.

18. An aqueous germicidal composition having improved stability against discoloration by light which comprises from about 0.1 percent to about 4 percent by weight of a halogenated phenolic germicide selected from the group consisting of 3,4',5-tribromosalicylanilide, 4,5-dibromosalicylanilide, and hexachlorophene, water, a solubilizer which is miscible in water and is also a solvent for the germicide, from about 1 percent to about 35 percent of a detergent, and a discoloration retarding amount of a discoloration inhibitor selected from the group consisting of alpha-phellandrene, allo ocimene, ocimene, terpinolene, myrcene, myrcene hydrate, rosin, tall oil, isoprene and abietic acid.

19. The composition according to claim 17 wherein the inhibitor is alpha-phellandrene, and is present at a level of 0.25 to 1 percent and the germicide is 3,4',5-tribromosalicylanilide, present at a level of about 0.4 percent.

20. A composition according to claim 17 wherein the germicide is 3,4',5-tribromosalicylanilide, present at a level of 0.4 percent and the inhibitor is myrcene, present at a level of 0.5 to 1 percent.

21. The composition according to claim 17 wherein the germicide is 3,4',5-tribromosalicylanilide, present at a level of 0.4 percent and the inhibitor is ocimene at a level of 0.25 to 1.0 percent.

22. The composition according to claim 17 wherein the germicide is 3,4',5-tribromosalicylanilide, present at a level of 0.4 percent and the inhibitor is abietic acid, present at a level of 0.1 to 0.5 percent.

* * * * *

PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,671,630 Dated June 20, 1972

Inventor(s) Francis Emery Carroll et al.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 1, line 68, "53" is misplaced;
Col. 2, line 19, change "2,867,688" to -- 2,867,668 --;
Col. 3, line 64, change "a" to -- as --;
Col. 4, line 43, change "allo ocimene, and" to
-- allo ocimene, ocimene, and --;
Col. 5, line 8, change "Sinpine 0" to -- Sinpine 0 0 --;
Col. 6, line 29, change "Ph" to -- pH --;
Col. 7, line 70, change"Nh_4" to -- NH_4 --;

Col. 8, line 26, change "Terpinyl" to -- Terpinyl acetate --;
Col. 9, line 67, change "TABS" to -- TBS --;
Col. 10, line 19, under 60 hrs., "0 hrs" unaligned;
Col. 10, lines 26-29, 30, "- - 2 2" unaligned;
Col. 10, line 29, under 30 hrs., "-" unaligned;
Col. 11, line 18, change "10.25" to -- 0.25 --;
Col. 12, line 72, under C', change "1" to -- 0 --;
Col. 13, line 32, "0 204" is unaligned and should be -- 204 --;
Col. 15, line 63, under J', change "1" to -- 0 --;
Col. 16, line 44, "0.10 0.25 0.50" unaligned;
Col. 16, line 70, "0" is unaligned;
Col. 17, line 18, change "acimene" to -- ocimene --.

Signed and sealed this 10th day of April 1973.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents