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ALKALINE GERMICIDAL CLEANER WITH COLOR INDICATOR

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This invention relates to germicidal cleaning compositions having colorimetric means for indicating duration of a minimum germicidally effective contact time. More particularly, the invention relates to dry powdered compositions in the form of mixtures of cleaning components, quaternary ammonium germicide, a per-compound as a source of releasable oxygen and an oxidizable dye, said compositions being readily soluble or dispersible in water to form colored, germicidal cleaning solutions which will maintain their color only for the limited time required for minimum effective germicidal contact with items being cleaned.

The concept of colored cleaning agents which will turn colorless in use is known in the art. In United States Patent No. 3,058,916 for example, there are disclosed laundry detergent compositions in solid form. In this patent, however, the dye is "merely intended to aid in the physical appearance of the product itself for marketing and sales purposes." The color disappears within the contemplated laundering cycle, but bears no useful relationship to the duration of such cycle.

Another United States Patent No. 2,498,343 discloses dry denture cleaning compositions containing oxygen yielding material and oxidizable dye supposedly providing an index of the proper length of time of the desired cleaning action upon the denture, with the color disappearance taking place within 10 to 30 minutes. Such a time interval is impractical, since a denture user will rarely want to wait around for 10 to 30 minutes for his teeth to be cleaned.

The present invention constitutes a distinct departure from these prior teachings in providing germicidal water-soluble powdered cleaning compositions in which colorimetric means is provided for indicating the duration of immersion in aqueous solutions thereof for proper germicidal treatment. The colorimetric means includes a combination of oxygen yielding material and a dye which loses its color rapidly through oxidation.

We have found the class of quaternary ammonium compounds to be the preferred germicides for this application in that these compounds are stable in the presence of the required amounts of alkali and oxidizing agents. The accepted quaternary ammonium germicides can be employed, including for example, benzethonium chloride, dodecyl benzyl trimethyl ammonium chloride, dodecyl benzyl diethyl ethanol ammonium chloride, cetyl pyridinium chloride and bromide, dodecyl benzyl triethanol ammonium chloride, N(lauroyl colamino-formylmethyl) pyridinium chloride, and dodecyl benzyl diethanol ammonium chloride. The quantity of germicide will vary to some extent depending on the intended use of the composition, but should generally be within the range of about 0.25 to 3% by weight of the composition. In an alkaline cleaner intended for use as a denture cleaner, the germicide concentration is preferably about 0.25 to 1.5%, whereas in an alkaline cleanser intended for home cleaning of sickroom utensils (glasses, dishes, silverware, etc. used by a patient) a somewhat higher concentration of germicide, suitably 2 to 3% should be employed.

The cleaning components which make up the bulk of

the compositions can be varied considerably, and in general, any alkaline cleaner can be used as a base for the new compositions. Typical components may include phosphates such as sodium phosphate, trisodium phosphate and tetra-sodium phosphate; carbonates such as sodium carbonate, calcium carbonate and magnesium carbonate, halide salts (particularly in denture cleaners) such as sodium chloride, and calcium chloride; borates such as boric acid and sodium borate; and oxygen releasing (peroxide) compounds such as perborates, persulfates, perphosphates, percarbonates and stabilized (e.g. coated granular form) sodium peroxide. In addition, the compositions may include 0.5 to 5.0% of an anionic surface active agent, such as sodium lauryl sulfate, or nonionic surface active agent, such as a condensate of ethylene oxide with polypropylene oxide (molecular weight 1501–1800) containing 80–90% by weight ethylene oxide, or a normally liquid alkyl phenol ethylene oxide condensate or polyoxyethylene ether alcohol solidified with about an equal weight of urea. The compositions can also be scented or flavored (in the case of denture cleaner) with a trace of suitable aromatic oils, such as peppermint oil, cinnamon oil, menthol, or vanillin.

The preparation of many alkaline cleansers employing combinations of the components noted above is described in Bennett's "Chemical Formulary," and in other standard references, and in adapting such known preparations to the present invention, two conditions must be satisfied. The pH of the composition in its intended use dilution should be within the range of about pH 10.5 to 11.5, and the amount of per-compound employed should be adjusted to the amount and type of dye to be employed as hereinafter described. The pH range is of importance in that we find that lower pH's tend to lengthen both the cleaning time and dye decoloration time.

The selection of a dye for use in the new compositions is greatly limited by the short time interval in which it must lose its color through oxidation. With the germicides employed, an effective germicidal action may be achieved in about 0.5 to 5 minutes, and the purpose of the dye is to provide a reliable indication to users of the compositions that treatment of objects, such as dentures, sickroom utensils, dishes, urinals, and the like, is continued for at least the interval required for complete germicidal effectiveness. Thus, for example, when handling sickroom utensils, they should be immersed in a freshly prepared colored solution of the composition, and left untouched until the color disappears. The cleaning solution and utensils can then be worked with, with the assurance that the danger of contamination or infection has been eliminated.

As a means for determining whether a dye will lose its color in a use solution within the desired time interval, the following screening test has been devised:

To 93 ml. of 0.1M trisodium phosphate solution at 37° C. (pH 11.5), add 2 ml. of 3% hydrogen peroxide solution and 5 ml. of a 0.01% dye solution, and note the time necessary for complete decolorization of the dye.

Dyes which give a measurable decoloration time of less than 5 minutes according to this test procedure are dyes which may be used in the new alkaline germicidal cleansers. (By measurable time is meant an interval of one second or more.) The actual decoloration time for a particular product can be adjusted by varying the pH within the range of 10.5 to 11.5, a lower pH generally prolonging the decoloration time.

In considering alkaline germicidal cleaners generally, the oxidizable dyes potentially useful in such compositions are relatively limited. In products to be used as denture cleaners, cleaners for sickroom utensils, and the like, however, the dye should be an F.D. & C. or D. & C. approved dye. The following tabulation shows the results of

11000—19999
20000—29999

screening a number of common dyes following the test procedure above described:

Dye:	CI	Decoloration time
F.D. & C. Blue No. 1	42090	2½ min.
F.D. & C. Blue No. 2	73015	2 sec.
F.D. & C. Yellow No. 8		>36 hrs.
F.D. & C. Yellow No. 5	19140	>36 hrs.
F.D. & C. Yellow No. 6	15985	4½ hrs.
F.D. & C. Green No. 1	42085	1 to 2 sec.
F.D. & C. Green No. 2	42095	1 to 2 sec.
F.D. & C. Green No. 3	42053	36 min.
F.D. & C. Red No. 1		>8 hrs.
F.D. & C. Red No. 2	16185	1 hr.
F.D. & C. Violet No. 1	42640	10 sec.
	42090	
D. & C. Blue No. 4		2 min.
D. & C. Blue No. 7	42090	2 min.
D. & C. Orange No. 4	15510	2½ hrs.
D. & C. Green No. 5	61570	>36 hrs.
D. & C. Red No. 19	45170	1½ hrs.
D. & C. Red No. 22	45380	1 hr.
D. & C. Red No. 28	45410	>36 hrs.
D. & C. Red No. 33	17200	>36 hrs.
Crystal Violet		1 to 2 sec.
Ext. D. & C. Orange No. 3		10 min.
Phenolphthalein		>8 hrs.

From the foregoing tabulation it follows that only 8 of these dyes are suitable for use in the compositions of the present invention, namely: F.D. & C. Blue No. 1, D. & C. Blue No. 4, D. & C. Blue No. 7, F.D. & C. Violet No. 1, F.D. & C. Blue No. 2, F.D. & C. Green No. 1, F.D. & C. Green No. 2, and Crystal Violet.

The temperature of 37° C. employed in the test procedure above described is selected as an approximate midpoint between room temperature and 50° C., the temperature range within which germicidal alkaline cleaners should generally be used. Within this temperature range the speed of decoloration increases as the temperature increases. At the same time, however, the rate of germicidal activity of the quaternary ammonium germicide is also increased as the temperature increases, and it has been found that the temperature coefficients for decoloration and germicidal activity are sufficiently close in the new compositions so that within the 35 to 50° C. temperature range at which the compositions will normally be employed, decoloration time, although changing, will indicate a substantially constant degree of germicidal activity.

It is to be understood that in use of the new compositions, the germicide remains active long after the dye has become decolorized and articles being treated can be kept immersed in cleaning solution for extended periods if desired. In many instances, however, the user will wish to minimize the cleaning time, and the presence of the oxidizable dye in the manner herein described provides a definite indication to the user of the minimum immersion time which will provide the desired germicidal action.

The amount of dye to be employed in an alkaline germicidal cleaner will depend upon the color intensity desired in the recommended use dilution of a particular product. This will generally require about 2 to 20 p.p.m. of dye in a use dilution, or about 0.01 to 0.1% in a composition intended to be used at a 2% concentration in use dilution. The amount of per-compound should be at least equivalent in active oxygen to the amount of hydrogen peroxide necessary to decolorize the dye within 5 min. under the conditions described in the "dye screening test." As the amount of per-compound is increased, the rate of decoloration of dye will increase, and adjustment of the amount of per-compound provides one means for "setting" the decoloration time for a product.

Further latitude in "setting" the decoloration time is also provided by adjusting the pH. By way of illustration, the following tabulation shows the difference in decoloration time of a particular dye (F.D. & C. Blue No. 1) due

to variation in pH. Except for pH adjustment (i.e. —0.1M Na_2HPO_4—NaOH soln.) the test procedure is the same as described above in the "dye screening test."

pH:	Decoloration time (F.D. & C. Blue No. 1) (Min.)
10.5	10
11.0	4
11.5	2½

The following examples will serve to show how typical alkaline germicidal cleaners in accordance with the present invention can be prepared, but it is to be understood that these examples are given by way of illustration and not of limitation:

The compositions of the following examples perform in substantially the same manner when the benzethonium chloride is replaced by an equivalent concentration of other quaternary ammonium germicides.

The compositions of the examples also perform in the same manner when the F.D. & C. Blue No. 1 is replaced by D. & C. Blue No. 4, or Blue No. 7, and shows substantially more rapid decoloration when the dye is replaced by F.D. & C. Violet No. 1, or F.D. & C. Blue No. 2.

EXAMPLE I

An alkaline germicidal cleaner is prepared by dry mixing the following components:

Component:	Parts by weight
Sodium chloride	17.725
Sequestrene	0.25
Sodium percarbonate	10.0
Sodium carbonate monohydrate	12.5
Tetrasodium pyrophosphate	15.0
Trisodium phosphate (12 H_2O)	37.5
Sodium N-methyl-N-oleoyl taurate (28% in NaCl)	4
Magnesium carbonate	2.5
Benzethonium chloride	0.4
F.D. & C. Blue No. 1	0.025
Flavor (peppermint oil)	0.1

This composition provides an effective denture cleaner when added to water at a concentration of about 2.5%. At this concentration the blue color disappears in about 3¾ min. at 37° C. and 1½ min. at 45° C. The pH of the use dilution is about 11.1.

EXAMPLE II

An alkaline germicidal cleaner is prepared by dry mixing the following components:

Component:	Parts by weight
Trisodium phosphate (12 H_2O)	30.0
Sodium tripolyphosphate	30.0
Sodium metasilicate	28.9
Benzethonium chloride	1.0
Sodium percarbonate	10.0
F.D. & C. Blue No. 1	.025

This composition provides an effective cleaner for sickroom utensils and dishes when added to water at a concentration of 1%. At this concentration the blue color disappears in approximately 4 min. at 37° C. The pH of the use dilution is 11.6.

Various changes and modifications in the alkaline germicidal cleaners with colorimetric indicator as herein disclosed will occur to those skilled in the art, and to the extent that such changes and modifications are embraced by the appended claims, they constitute part of the present invention.

We claim:

1. An alkaline germicidal cleaning composition having indicator means to signify the minimum contact time for effective germicidal action in use dilutions thereof, said composition consisting essentially of a mixture of inorganic alkaline cleaning components providing a pH of

10.5 to 11.5 in aqueous use dilution containing amounts of the order of 1.0 to 2.5% by weight of said composition, 0.25 to 3% of a quaternary ammonium germicide selected from the group consisting of benzethonium chloride, dodecyl benzyl trimethyl ammonium chloride, dodecyl benzyl diethyl ethanol ammonium chloride, cetyl pyridinium chloride and bromide, dodecyl benzyl triethanol ammonium chloride, N(lauroyl colaminoformylmethyl)pyridinium chloride, and dodecyl benzyl diethanol ammonium chloride, 0.01 to 0.1% of a water soluble dye selected from the group consisting of F.D. & C. Blue No. 1, D. & C. Blue No. 4, D. & C. Blue No. 7, F.D. & C. Violet No. 1, F.D. & C. Blue No. 2, F.D. & C. Green No. 1, F.D. & C. Green No. 2, and Crystal Violet, and an oxygen releasing inorganic per-compound in an amount to decolorize said dye in such use dilution in a time interval of 0.5 to 5 minutes, said inorganic per-compound being selected from the group consisting of perborates, persulfates, perphosphates, percarbonates, and stabilized (granular coated) sodium peroxide.

2. An alkaline germicidal cleaning composition as defined in claim **1**, wherein the dye employed is F.D. & C. Blue No. 1.

3. An alkaline germicidal cleaning composition as defined in claim **1**, wherein the dye employed is D. & C. Blue No. 4.

4. An alkaline germicidal cleaning composition as defined in claim **1**, wherein the dye employed is D. & C. Blue No. 7.

5. An alkaline germicidal cleaning composition as defined in claim **1** wherein the *W/W* ratio of per-compound to dye is of the order of 400:1.

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