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COMPOSITIONS COMPRISING QUATERNARY AMMONIUM GERMICIDES AND NONIONIC SURFACTANTS

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ABSTRACT OF THE DISCLOSURE

Compositions comprising quaternary ammonium germicides and nonionic detergents wherein unique compatibility with respect to performance of the quaternary ammonium germicides is achieved in the presence of amounts of detergent which are at least twice the amount of germicide, by employing a nonionic detergent in which the major portion of the molecule is made up of block polymeric C_2 to C_4 alkylene oxides, with alkylene oxide blocks containing C_3 to C_4 alkylene oxides and 0–45% ethylene oxide providing a significant hydrophobic function, and alkylene oxide blocks containing ethylene oxides and 0–45% of C_3 to C_4 alkylene oxide providing a significant hydrophilic function.

Preferred compositions are detergent sanitizers containing quaternary ammonium germicides in combination with 5 to 10 times as much detergent. In such compositions enhanced and extended germicidal action can be provided by employing as the nonionic detergent component a detergent-iodine complex, or by adding a PVP-iodine complex.

BACKGROUND OF THE INVENTION

With the commercial introduction of quaternary ammonium germicides (germicidal quats) about 25 years ago, the desirability of combining germicidal quates with detergents in the formulating of disinfecting and sanitizing products was immediately apparent. The then available anionic detergents were tried and found unsuitable in such combinations due to reaction with the quaternary ammonium compound. When nonionic detergents became commercially available, it was initially thought that detergent-sanitizer compositions could be prepared with quaternary ammonium germicides and varying amounts of nonionic detergent.

The recognition that germicidal quats are adversely affected by hard water came only shortly after the introduction of these chemicals of phenomenally high "phenol coefficient." Early literature on the subject of combinations of quats and nonionics was marked by conflicting reports from reputable laboratories in which similar ratios of nonionic to quat were shown to be effective or ineffective for apparently similar uses. The situation was complicated by the tendency to measure disinfecting properties under prolonged kill time or stasis conditions. Not only was water hardness frequently not considered as a factor, but the added effect of nonionic interference in the presence of hard water was not recognized. Some investigators, working with distilled water, found that nonionic detergents could increase germicidal performance of quats under certain conditions, especially where prolonged kill times were used.

More recently, quat manufacturers found that certain quats were more resistant to hard water than others. During this time official government agencies began to recognize the need for fast killing detergent-quat performance in the presence of hard water. The official performance test for detergent-sanitizers (e.g. nonionic-quat formulations) is given in the AOAC Tenth Edition, 1965, paragraphs 5.023 to 5.032 inclusive. This test prescribes a 30 second performance end point under hard water test conditions.

Quat manufactures, who acutally participated in the development of this method through industry-regulatory agency cooperation, quickly put a ceiling on the amount (ratio) of nonionic which could be used with quats. This ceiling, universally adopted by the trade for the past ten years, places a limit of from 1.5 to 2.0 parts of nonionic to one part of quat in a detergent-sanitizer formulation. At the same time, a minimum of 200 p.p.m. quat was, and is now, generally accepted as being the least amount of quat which can be safely recommended in a detergent-sanitizer use dilution based on a conventional nonionic and germicidal (even "hard water") quat. This means, in effect, that use concentrations containing 200 p.p.m. quat limited to 400 p.p.m. of detergent are significantly below the generally recognized level of about 1000 p.p.m. (0.1%) of nonionic, which is necessary for light duty hard surface detergency. For many difficult cleaning jobs, ten times this amount of detergent is indicated. At the present time, therefore, quat-nonionic detergent-sanitizers are not used for this purpose in part because of the prohibitive cost of the concomitant quat germicide. For example, at today's prices, germicidal quats cost from 5 to 10 times as much as the widely used nonionic detergents.

THE INVENTION

The present invention resides in the discovery that the expected interference of nonionic detergent with germicidal quats can be avoided, paving the way for the formulating of compositions containing both germicidal quats and nonionic detergents without the traditional limitation on the proportions of components, by selecting the detergent from a limited class of nonionic detergents in which the major portion of the molecule is made up of block polymeric C_2–C_4 alkylene oxides, with alkylene oxide blocks containing C_3 to C_4 alkylene oxides and 0–45% ethylene oxide providing a significant hydrophobic function, and alkylene oxide blocks containing ethylene oxide and 0–45% of C_3 to C_4 alkylene oxide providing a significant hydrophilic function. Such detergents, while preferably built up from an alkylene oxide chain starting group, can have as a starting nucleus almost any active hydrogen containing group including, without limitation, amides, phenols, and secondary alcohols.

The reason for the unique compatibility of the type nonionic detergents above described with germicidal quats is not understood, but it appears to be in some way tied to the block polymer nature of the detergents and particularly to the presence of a C_3 to C_4 alkylene oxide block or a mixed ethylene oxide and C_3 to C_4 alkylene oxide block providing a significantly hydrophobic function in the detergent. Samples of various known detergents answering this description have consistently been found to perform satisfactorily in the new type compositions and to contrast sharply with more conventional nonionic detergents.

One group of detergents containing the characteristic block polymer of propylene oxide, and commercially available under the trademark "Pluronic" can be represented by the formula:

Formula A

$$HO(EO)_x(PO)_y(EO)_{x'}\text{—}H$$

where EO and PO represent ethylene oxide and propylene oxide respectively, y equals at least 15, $(EO)_{x+x'}$ equals 20 to 90% of the total weight of said compound, and the molecular weight is in the range of about 2000 to 15,000. Typical Pluronics which will hereinafter be referred to are:

	Approximate molecular weight	Wt. percent EO
Detergent:		
Pluronic L44	2,200	40–50
Pluronic P54	2,650	40–50
Pluronic P65	3,500	50–60
Pluronic L62	2,500	20–30
Pluronic P85	4,600	50–60
Pluronic P105	6,350	50–60
Pluronic P123	5,650	30–40
Pluronic F108	15,000	80–90

Another group of detergents appropriate for use in the new compositions can be represented by the formula:

Formula B

$$\text{Alkoxy } (EO,PO)_a(EO,PO)_b\text{—}H$$

wherein the alkoxy group contains 1 to 20 carbon atoms, the weight percent of EO is within the range of O to 45% in one of the blocks *a*, *b*, and within the range of 60 to 100% in the other of the blocks *a*, *b*, and the total number of moles of combined EO and PO is in the range of 6 to 125 moles, with 1 to 50 moles in the PO rich block and 5 to 100 moles in the EO rich block.

Typical detergents falling within Formula B above which may be employed in the new compositions include the following, identified in terms of the stated values for the different variables in the formula:

	Carbon in alkoxy	Wt. percent in "a"	EO in "b"	Moles EO plus PO in "a"	Moles EO plus PO in "b"
Detergent:					
a	14	25	75	4.0	13.7
b	14	75	25	13.7	4.0
c	15	25	75	4.3	14.6
d	14	15	85	3.9	14.0
e	13.5	33	67	2.7	12.4
f	18	25	75	5.0	15.0
g	15	30	70	2.1	14.0

Other examples of detergents of the general type embraced by Formula B include: Tergitol XD, Tergitol XH, and Tergitol X60 which are butoxy derivatives of propylene oxide, ethylene oxide block polymers having molecular weights within the range of about 2000–5000.

Other suitable detergents generally related to the above formulae, but containing polymeric butoxy (BO) groups can be represented as follows:

Formula C

$$RO(BO)_n(EO)_x\text{—}H$$

wherein R is an alkyl group containing 1 to 20 carbon atoms, n is about 15 and x is about 15; and

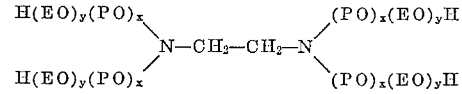
Formula D

$$HO(EO)_x(BO)_n(EO)_y\text{—}H$$

wherein n is about 15, x is about 15 and y is about 15.

Still other suitable detergents are ethoxylated derivatives of propoxylated ethylene diamine, available as "Tetronics and characterized as follows:

Formula E



where (EO) and (PO) are ethoxy and propoxy respectively, the amount of $(PO)_x$ is such as to provide a molecular weight prior to ethoxylation of about 300 to 7500, and the amount of $(EO)_y$ is such as to provide about 20% to 90% of the total weight of said compound.

The examples hereinafter appearing are directed essentially to comparisons between compositions in which conventional germicidal quats are associated with various nonionic detergents embraced by Formulas A to E, and with other common nonionic detergents which are in extensive commercial use. Such conventional germicidal quats, some of which will be referred to in the examples include the following, identified by trade name and chemical composition. Those identified with the asterisk * are generally recognized as "hard water" quats.

Cationic germicide:	Composition
Hyamine 2389	Methyl dodecylbenzyl trimethyl ammonium chloride, and methyl dodecyl xylylene bis (trimethyl) ammonium chloride.
Beloran	Lauryl benzyl diethanolammonium chloride.
*Tetrosan 3, 4 D	Alkyl dimethyl 3, 4 dichlorobenzyl ammonium chloride.
*BTC 471	Alkyl** dimethyl ethylbenzyl ammonium chloride ** C_{12} 50%, C_{14} 30%, C_{16} 17%, C_{18} 3%.
*BTC 927	Alkyl** dimethyl dimethylbenzyl ammonium chloride ** C_{12} 50%, C_{14} 30%, C_{16} 17%, C_{18} 3%.
*BTC 1100	Alkyl** dimethyl 1-naphthylmethyl ammonium chloride monohydrate ** C_{12} 98%, C_{14} 2%.
Emcol E607	N(lauroyl colaminoformylmethyl) pyridinium chloride.
*Hyamine 3500	N-alkyl (C_{12}, C_{14}, C_{16}) dimethyl benzyl ammonium chloride.
Cetab	Cetyltrimethylammonium bromide.
CPC	Cetylpyridinium chloride.
LPC	Laurylpyridinium chloride.
Hyamine 1622	Diisobutyl phenoxy ethoxy ethyl dimethylbenzyl ammonium chloride.

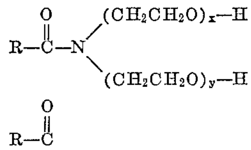
For comparison purposes the examples include data for compositions employing a number of common nonionic detergents which are outside the scope of the invention, having the trade designations and chemical identifications as follows:

Igepal CO–710	Nonyl phenol-ethylene oxide condensate with 10–11 moles of ethylene oxide.
Igepal CO–880	Nonyl phenol-ethylene oxide condensate with about 30 moles of ethylene oxide.
Igepal CO–990	Nonyl phenol-ethylene oxide condensate with about 100 moles of ethylene oxide.

Igepal AR660 ------ Polyoxyethylene* fatty alkyl** ether * 60–65% ethylene oxide ** C_{12}–C_{18} (av. C_{14}) alkyl.

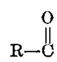
Triton X–100 ------ Octyl phenol-ethylene oxide condensate with about 10 moles of ethylene oxide.

Ethomid C/15 -----



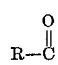
from coco fatty acids $x+y=5$.

Ethomid HT60 ----- As above



from hydrogenated tallow $x+y=50$.

Ethomid HT15 ------ As above



from hydrogenated tallow $x+y=5$.

Brij 35 ------------ Polyoxyethylene (23) lauryl ether.

Brij 78 ------------ Polyoxyethylene (20) stearyl ether.

Myrj 45 ----------- Polyoxyethylene (8) stearate.

Myrj 53 ----------- Polyoxyethylene (50) stearate.

Amine oxide "A" -- Lauryl dimethyl amine oxide.

Amine oxide "B" -- Myristyl dimethyl amine oxide.

In the examples germicidal activity is measured by one of the following test procedures:

Procedure A.—The test procedure described in "Official Methods of Analysis of the Association of Official Agricultural Chemists," Tenth Edition (1965) pp. 87–89 and page 80.

Procedure B.—The following procedure, which involves slight modification of Procedure A:

The test solution is prepared by appropriate dilution of a sample in water of specific hardness (page 88). A sterile 250 ml. erlenmeyer flask containing 99 ml. of the test solution is placed in a 20° C. constant temperature water bath, and the solution is brought to temperature. A 24-hour culture of S. choleraesuis ATCC No. 10708 grown in AOAC broth (page 80) is used as the test culture. This culture meets the AOAC requirements for phenol resistance, i.e., it is killed by a 1:90 dilution of phenol in 10 minutes, but not in 5 minutes, and it resists a 1:100 dilution of phenol for 15 minutes.

One ml. of the test culture is added to 99 ml. of the test solution held at 20° C. At the end of specified time intervals (30 sec., 1 min., 2 min.), 1 ml. of the culture-solution mixture is removed and diluted in 9 ml. Letheen neutralizer blank (page 87). One ml. and 0.1 ml. amounts of this neutralizer dilution are plated in duplicate in Tryptone Glucose Extract Agar containing Letheen (page 87) as a neutralizer. The plates are incubated at 37° C. for 48 hours. At the end of this time, the resultant colonies are counted. The average counts per ml. when multiplied by the above dilution made prior to plating gives the number of surviving organisms per ml. of germicidal test solution.

The actual number of organisms (the challenge) originally subjected to the action of the test solution is determined at the same time as follows: One ml. of the test culture is added to 99 ml. of phosphate buffer (pH 7.2) dilution water (page 87) held at 20° C. At the end of 30 seconds, 1 ml. of the culture-buffer mixture is transferred serially to 3 bottles containing 100 ml. each of phosphate buffer dilution water. The final dilution is plated in duplicate in 1 ml. and 0.1 ml. amounts in Tryptone Glucose Extract Agar, and the resultant colonies counted. The average counts per ml. when multiplied by the above dilution figure give the number of organisms (the challenge) actually subjected to the action of the test solution. A comparison of this challenge count with the number surviving in the test solution is the basis for calculating the percent reduction achieved by the test solution.

EXAMPLE I

In standard 500 p.p.m. hard water germicidal detergent solutions were prepared containing 200 p.p.m. of "Hyamine 3500" and amounts of different nonionic detergents. These were tested by Procedure B above described using 1 ml. *S. cholerasuis* broth in 100 ml. of test solution (3,000,000 organisms per ml. of test solution) and plate counts determined at ½ min., 1 min., and 2 min. intervals. The results obtained are as follows:

Detergent	Ratio det./quat	Plate count, minutes ½	1	2
None		<10	<10	<10
Igepal CO-710	2/1	25,000	3,000	170
Do	5/1	1,000,000	500,000	100,000
Pluronic P65	5/1	<10	<10	<10

Essentially the same results are obtained when the amount of "Pluronic P65" is increased to 10/1 or even to 100/1. Note in this connection that as optimum proportions for most practical detergent sanitizer compositions, the detergent/quaternary ratio should be in the 5/1 to 10/1 range.

EXAMPLE II

Following the same procedure as described in Example I using 500 p.p.m. hard water, solutions containing 200 p.p.m. of "Beloran" (which is not a hard water quat) and various detergents in the amounts indicated were prepared and tested with the following results:

Detergent	Ratio det./quat	Plate count, minutes ½	1	2
None		14,000	1,400	10
Igepal CO-710	2/1	1,000,000	50,000	2,500
Do	5/1	1,000,000	>1,000,000	>1,000,000
Pluronic L44	5/1	13,000	1,600	30
Pluronic P54	5/1	12,500	360	10
Pluronic P65	5/1	12,800	1,100	10
Pluronic L62	5/1	26,400	1,400	20
Pluronic P85	5/1	6,000	400	<10
Pluronic P105	4/1	64,000	7,200	110
Tergitol XD	4/1	7,300	350	10
Tergitol XH	4/1	26,000	700	20
Ethomid C/15	5/1	>1,000,000	640,000	320,000
Ethomid HT60	5/1	>1,000,000	700,000	28,000
Igepal CO-880	5/1	>1,000,000	780,000	180,000
Igepal CO-990	5/1	360,000	13,000	700
Brij 35	5/1	>1,000,000	>1,000,000	>1,000,000
Brij 78	5/1	1,000,000	1,000,000	1,000,000
Myrj 45	3/1	660,000	150,000	8,400
Myrj 53	3/1	>1,000,000	>1,000,000	25,000
Igepal AR660	5/1	>1,000,000	>1,000,000	>1,000,000

In the foregoing tabulation it should be pointed out that "Igepal CO-990" which shows what might be considered borderline performance at the 5/1 detergent/quaternary ratio should be disregarded because this material contains so much ethylene oxide that it is no longer useful as a detergent.

EXAMPLE III

Following the same procedure as described in Example I, but preparing solutions in 300 p.p.m. hard water, solutions containing 200 p.p.m. of different cationic germicides and the indicated amounts of different nonionic detergents were prepared and tested, giving the results shown in the following tabulations:

Composition tested	Plate counts, minutes		
	½	1	2
Hyamine 3500 alone	<10	<10	<10
Plus 2/1 Igepal CO-710	12,300	170	50
Plus 5/1 Igepal CO-710	>1,000,000	468,000	103,000
Plus 5/1 Pluronic P65	<10	<10	<10
Beloran alone	1,550	25	<10
Plus 2/1 Igepal CO-710	84,500	6,000	240
Plus 5/1 Igepal CO-710	820,000	470,000	145,000
Plus 5/1 Igepal AR660	>1,000,000	880,000	310,000
Plus 5/1 Pluronic P65	570	10	<10
Emcol E607 alone	62,500	5,200	1,700
Plus 2/1 Igepal CO-710	410,000	195,000	65,000
Plus 5/1 Igepal CO-710	>1,000,000	>1,000,000	>1,000,000
Plus 5/1 Pluronic P65	71,000	3,500	710
Hyamine 2389 alone	270,000	108,000	27,000
Plus 5/1 Igepal CO-710	>1,000,000	>1,000,000	900,000
Plus 5/1 Pluronic P65	520,000	135,000	95,000

The foregoing tabulation is of special interest in showing a substantial variation in activity of the germicide alone, from the very quick acting "Hyamine 3500" to the much slower acting (but widely used commercially) "Hyamine 2389." The advantage of "Pluronic P65" over "Igepal CO-710" at the 5/1 detergent/quaternary level is quite apparent with each of the germicides, in spite of the differing activities of the germicides per se.

EXAMPLE IV

Detergent-germicide solutions were prepared in 500 p.p.m. hard water using as germicide 200 p.p.m. of "Tetrosan 3,4 D" and varying amounts of different detergents as indicated. The resulting solutions were tested for germicidal activity by Procedure A above described using *E. coli* as the test organism. The comparative results, at 30 sec. and 1 min., expressed in plate count and percent, reduction in the number of organisms, for the germicide alone and the germicide plus detergent under the varied conditions are as follows:

Detergent	Ratio det./quat	30 seconds		1 minute	
		Count	Percent reduction	Count	Percent reduction
None		<10	>99.999	<10	>99.999
Igepal CO-710	2/1	>1,000,000	<98.9	>1,000,000	<98.9
Do	5/1	>1,000,000	<98.9	>1,000,000	<98.9
Pluronic P65	2/1	190	>99.999	<10	>99.999
Do	5/1	<10	>99.999	<10	>99.999

EXAMPLE V

A number of solutions were prepared in water of different hardness as indicated, containing "Hyamine 3500" alone at the 200 p.p.m. level, and Hyamine 3500 plus 2/1, 5/1 and 10/1 ratios of different type detergents. These were tested by Procedure B above described for 1 minute kill, and the plate counts of surviving organisms are tabulated below.

Detergent	Ratio det./quat	Plate count at water hardness indicated, one minute kill			
		500 p.p.m.	300 p.p.m.	100 p.p.m.	0 p.p.m.
None		<10	<10	<10	<10
Igepal CO-710	2/1	3,000	170	<10	<10
Do	5/1	500,000	470,000	44,000	<10
Do	10/1	>1,000,000	>1,000,000	>1,000,000	<10
Pluronic P65	2/1	<10	<10	<10	<10
Do	5/1	<10	<10	<10	<10
Do	10/1	<10	<10	<10	<10

These results show how the conventional nonionic destroys the quat activity as a function of ratio of nonionic to quat, which is the basis for the present art ceiling of two parts of nonionic for one part of quat. The results also show how the conventional nonionic becomes increasingly destructive to quat activity at concentrations needed for cleaning as the water hardness increases. This is in sharp contrast to the results found in the case where block polymer nonionics are substituted for conventional nonionics, in which case the number of surviving organisms were equivalent to the quat alone; that is, there was no interference with quat kill under these conditions.

EXAMPLE VI

A number of solutions were prepared in water of different hardness, as indicated, containing 200 p.p.m. of Hyamine 3500 and detergents in the proportions indicated; and these solutions were tested according to Procedure A above using *E. coli* as the test organism with the following results expressed in percent reduction in the number of organisms:

Detergent	Ratio det./quat.	Hard water, p.p.m.	Result	
			30 sec.	1 min.
None		500	(1)	----------
Igepal C0710	2/1	500	(2)	(2)
Do	2/1	300	(2)	99.8
Do	2/1	200	(2)	99.991
Do	2/1	100	99.998	>99.999
Do	2/1	50	(1)	----------
Do	1/1	300	99.987	>99.999
Do	1/1	100	99.993	>99.999
Do	1/2	300	(1)	----------
Amine oxide "A"	2/1	200	(2)	(2)
Amine oxide "B"	2/1	200	(2)	(2)
Do	2/1	100	99.724	99.844
Do	2/1	50	99.758	99.996
Do	1/1	100	99.998	>99.999
Do	1/2	100	(1)	----------

1 Passes.
2 Too numerous to count.

These results indicate clearly the effect of both water hardness and detergent/quat ratio on the germicidal activity in the presence of these conventional detergents. The results here are given for both the 30 second and 1 minute kill merely to enable better visualizing of these effects. It should be noted, however, that to "pass" the test Procedure A there must be at least a 99.999% reduction in the number of organisms in 30 seconds; and in the following examples "passing" and "failing" results have reference only to the 30 sec. test.

EXAMPLE VII

A number of solutions were prepared in 200 p.p.m. hard water containing 200 p.p.m. of Hyamine 3500 and 400 p.p.m. (2/1 detergent/quat ratio) of various conventional detergents and block polymer detergents, and these solutions were tested according to test Procedure A.

The solutions containing the conventional detergents Igepal CO-710, Myrj 78, Ethomid HT 15, Amine Oxide "A" and Amine Oxide "B" all failed to pass this test.

The solutions containing the block polymer detergents Pluronics P65, P85, P105, F108 and P123, Tergitol XH, and Tetronic 704 (a compisition according to Formula E in which the molecular weight prior to ethoxylation is 2500–3000, and the molecular weight of the ethylene oxide is 1600–2000) all passed the test. Also passing the test were solutions in which the block polymers are identified as follows:

Block polymer "A".—a compound of the formula $HO(C_3H_6O)_x(C_2H_4O)_y(C_3H_6O)_xH$ having a molecular weight of approximately 4000 with equal parts by weight of ethylene oxide and propylene oxide.

Block polymer "B".—a compound similar to the "Pluronics" of Formula A in which the hydrophobe y contains about 90% PO and 10% EO and has a molecular weight of about 2500 and the hydrophile $x+x'$ contains about 90% EO and 10% PO and has a molecular weight of about 1700.

Block polymer "C".—a compound similar to Block polymer "B" in which both hydrophobe and hydrophile have molecular weights of about 2500.

EXAMPLE VIII

A number of solutions were prepared in water of different hardness, as indicated, containing 200 p.p.m. of Tetrosan 3, 4 D and different detergents of the conventional type and the block polymer type in the proportions indicated. These solutions were tested according to Procedure A above using *E. coli* as the test organism with the following results:

	Ratio det./quat	Hard water, p.p.m.	Result
Conventional detergents:			
None		500	Passes.
Igepal C0710, 400 p.p.m.	2/1	200	Fails.
Igepal C0710, 1,000 p.p.m.	5/1	50	Do.
Igepal C0730, 400 p.p.m.	2/1	200	Do.
Triton X-100, 400 p.p.m.	2/1	200	Do.
Amine oxide "A", 400 p.p.m.	2/1	200	Do.
Block Polymer Detergents:			
Pluronic F68, 400 p.p.m.	2/1	500	Passes.
Pluronic P65, 1,000 p.p.m.	5/1	500	Do.
Pluronic P65, 4,000 p.p.m.	20/1	300	Do.
Pluronic L64, 25,000 p.p.m.	125/1	100	Do.

EXAMPLE IX

The procedure of Example VIII was repeated using a different quaternary ammonium compound, BTC 471, at the 200 p.p.m. level, and a number of conventional type detergents and block polymer detergents in the amounts indicated. Testing of the solutions according to Procedure A gave the following results:

	Ratio det./quat	Hard water, p.p.m.	Result
Conventional detergents:			
None		800	Passes.
Igepal C0710, 400 p.p.m.	2/1	300	Fails.
Myrj 53, 400 p.p.m.	2/1	300	Do.
Bryj 78, 400 p.p.m.	2/1	300	Do.
Ethomid HT15, 400 p.p.m.	2/1	500	Do.
Amine oxide "A", 400 p.p.m.	2/1	300	Do.
Amine oxide "B", 400 p.p.m.	2/1	300	Do.
Triton X-100, 400 p.p.m.	2/1	300	Do.
Block Polymer detergents:			
Pluronic P65, 400 p.p.m.	2/1	300	Passes.
Do	2/1	800	Do.
Pluronic P65, 4,000 p.p.m.	20/1	500	Do.
Block, Polymer D, 400 p.p.m.	2/1	300	Do.
Block Polymer E, 400 p.p.m.	2/1	300	Do.

In the foregoing tabulation Block Polymer D is a nonionic detergent identified by Formula B(a) and Block Polymer E is identified by Formula B(g).

EXAMPLE X

The Procedure of Example VIII was repeated using as quaternary ammonium compounds:

A—BTC 927 at 200 p.p.m.
B—BTC 1100 at 200 p.p.m.

and typical conventional type and block polymer type detergents in the amounts indicated. Testing of the solutions according to Procedure A gave the following results:

Quat	Detergent	Ratio det./quat	Hard water, p.p.m.	Result
A	None		300	Passes.
B	do		300	Do.
	Conventional detergents:			
A	Igepal C0710 at 400 p.p.m.	2/1	300	Fails.
B	do	2/1	300	Do.
	Block polymers:			
A	Pluronic P65 at 400 p.p.m.	2/1	300	Passes.
A	Pluronic P65 at 4,000 p.p.m.	20/1	300	Do.
B	Pluronic P65 at 400 p.p.m.	2/1	300	Do.

In the formulating of germicidal detergent sanitizer products using quaternary ammonium germicides it is frequently desirable to include added components such as builders, pH regulating additives, and/or organic sequestering agents. It has been found that such additives can be used in formulating products containing block polymer type detergents of the present invention. This is demonstrated in the following example:

EXAMPLE XI

A solution containing 200 p.p.m. of Hyamine 3500 and 500 p.p.m. of Pluronic P65 (2.5/1 ratio of detergent/quat) in 200 p.p.m. hard water readily passes the Official AOAC germicidal and Detergent Sanitizer Test—Procedure A.

Similar solutions were prepared containing additive in the amounts indicated and these were tested according to Procedure A with the following results:

Additive			
Type	Concentration, p.p.m.	Solution, pH	Result
Na_2CO_3	400	11	Passes.
H_3PO_4	400	3	Do.
EDTA [1]	200	10.8	Do.
STPP [2]	200	10.8	Do.

[1] Ethylene diamine tetraacetic acid sodium salt.
[2] Sodium tripolyphosphate.

The results when using the block polymeric material Pluronic P65 in the foregoing examples are characteristic of block polymer detergents generally as embraced by Formulas A to E above. While there may be some variation in organism kill obtained when switching from one block polymer to another as indicated in Example II or when switching from one cationic material to another as indicated in Example III, the use of block polymer detergents permits extensive variation of the detergent/quat ratio and of the water hardness without the severe restriction in the functioning of the germicide which is characteristic of ordinary nonionic detergents.

The foregoing examples have clearly demonstrated the unusual freedom from interference with the germicidal quat by the special block polymeric nonionic detergents herein described when the detergent: quat ratio is equal to or greater than 2:1, and even as high as 100:1. There is special value in being able to provide a nonionic detergent: germicidal quat ratio in the range of about 5:1 to 10:1 since this permits a combination of optimum germicidal action and optimum hard surface detergency in a single composition. The term germicidal quat as here used is understood to embrace any quaternary ammonium compound recognized as having germicidal activity of practical significance. As a class such quaternary ammonium compounds are characterized as having at least one long chain alkyl or aryl group of 8 to 22 carbon atoms joined to the quaternary nitrogen. Furthermore, germicidal activity which is of "practical significance" requires that the quaternary ammonium compound have a phenol coefficient of at least 50, and preferably at least 100, with respect to *S. aureus* and *S. typhosa* at 20° C.

The preceding examples have demonstrated the superiority of block polymer nonionic detergents in situations where hard water is a factor. The present invention, however, extends into areas where distilled water is used as the testing medium. The most important official test method for testing disinfactants to determine the maximum dilution which is effective for practical disinfection is called the Use-Dilution Method. This method is described on pages 82–84 of AOAC (1965) previously cited. Distilled water is used as the test medium.

By the way of background, it should be pointed out that the minimum amount of the most active quaternary ammonium compound accepted as passing this test is 400 p.p.m. When formulating end use products with detergents, builders, pH regulating additives, and/or organic sequestering agents for purposes of better cleaning, the quat level may actually have to be increased, so that as much as 500 p.p.m. of quat are necessary.

It has now been found that in contrast to such adverse performance in the presence of conventional detergent, germicidal quats become more effective when combined with the block polymer nonionic detergents of the present invention. This is clearly demonstrated in the following example:

EXAMPLE XII

Solutions were prepared in distilled water using Hyamine 3500 as the quat, two block polymer detergents, one conventional detergent and certain other additives in the amounts indicated; and the solutions were tested by the Use Dilution Method above mentioned with the following results

Amounts in parts per million, p.p.m.							
Hyamine 3500	Pluronic P65	Pluronic P123	Igepal CO710	STPP	Na_2CO_3	EDTA	Results
400							Passes.
300							Fails.
300				50	400	50	Do.
300			600	50	400	50	Do.
300	600			50	400	50	Passes.
300		600		50	400	50	Do.

In utilizing the present invention to formulate commercial products in the field of detergent-sanitizers, it is within the scope of the present invention not only to combine compatible acids and alkaline substances as normally employed in such products, but also to employ other compatible active components in such products.

By way of illustration, in the detergent sanitizer field it is frequently desired to have a single product both long sustained germicidal action and rapid kill of organisms. Some of the germicides which are most desirable for the sustained germicidal action are too slow acting for the desired rapid kill performance. This problem can be met by supplying the nonionic detergent as a detergent-iodine complex. The rapid kill germicidal activity of nonionic detergent-iodine complexes is well recognized in the art and some of the nonionics embraced by Formulas A to E have been employed in detergent iodine products as detergent-sanitizers and the like.

The block polymeric nature of the nonionic detergents embraced by Formulas A to E makes them inherently capable of complexing with iodine, and while not all of the detergents would be detergents of choice for straight detergent-iodine compositions, it is considered that any of the disclosed nonionic detergents supplied as an iodine complex would effectively supplent the activity of the germicidal quat.

In such a dual purpose detergent sanitizer the amount of iodine present is preferably about 1 to 2 times the amount of germicidal quat, with the optimum amount in each instance being dependent upon the relative activity of the germicidal quat and the physical stability of the inherently complex formulation.

The following example illustrates a typical detergent-sanitizer composition of the present invention containing both germicidal quat and iodine.

EXAMPLE XIII

A detergent sanitizer is prepared by combining:

Component:	Percent by weight
Pluronic P–123	10.0
HI—I_2 (57% I_2)	3.0
Isopropanol	5.0
Propylene glycol	10.0
Sodium dodecyl benzene sulfonate (90% act.)	5.0
Tetrosan 3,4 D (60% act.)	2.5
Phosphoric acid (75%)	10.0
Water	54.5
	100.0

The HI—I_2 is first mixed with the Pluronic. The other components are then added in the order listed and mixed until a uniform clear dark-brown colored solution is obtained, the entire mixing being effected at room temperature.

This composition is a multipurpose detergent-sanitizer currently being readied for commercial distribution.

At 1:50 dilution in waters of normally varying hardness it is an excellent heavy duty cleaner-sanitizer.

At 1:200 dilution the composition provides a good general purpose detergent-sanitizer, which passes the Use Dilution Confirmation Test A.O.A.C. (1965) pages 82–84.

In this composition the major germicidal activity is the rapid activity which is provided by the iodine. The germicidal quat, however, fills an important role. It provides a continuing germicidal action on surfaces coated with the composition.

EXAMPLE XIV

A detergent sanitizer is prepared containing:

Component:	Percent by weight
Pluronic P–123	10.0
HI—I_2(57% I_2)	1.75
Tetrosan 3,4 D (60% act.)	1.8
PVP (polyvinylpyrrolidone)	5.0
Water	81.45

The order of mixing is not critical. The HI—I_2 can be first mixed with the Pluronic and the other components added, or the HI—I_2 can be mixed with the PVP aqueous solution and the other components added. Either procedure leads to a similar distribution of complexed iodine between the Pluronic and the PVP.

This is a stable product which readily dilutes to practical use solutions. At a 1:100 dilution it is an effective general purpose detergent sanitizer.

The various examples have shown block polymer nonionic detergents with as few as 2 or 3 and as many as 8 blocks per molecule. The number of blocks appears to be immaterial, and detergents with intermediate numbers of blocks or higher numbers, as well as a greater number of alternating blocks are within the scope of the invention provided these blocks provide the essential hydrophobic and hydrophilic functions previously described.

Various changes and modifications in the versatile compositions of block polymeric nonionic detergents and germicidal quats 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, it is to be understood that they constitute part of the present invention.

We claim:

1. A germicidal detergent composition consisting essentially of a germicidal quaternary ammonium compound and a nonionic detergent in which the major portion of the molecule is made up of block polymeric C_2 to C_4 alkylene oxides, with alkylene oxide blocks containing C_3 to C_4 alkylene oxides and 0–45% ethylene oxide providing a significant hydrophobic function, and alkylene oxide blocks consisting of ethylene oxide and 0–45% of C_3 to C_4 alkylene oxide providing a significant hydrophilic function, the nonionic detergent being a member selected from the group consisting of the following formulae:

(A) $HO(EO)_x(PO)_y(EO)_{x'}—H$

wherein EO and PO represent ethylene oxide and proylene oxide, respectively, y equals at least 15, $(EO)_{x+x'}$ equals 20–90% of the total weight of said compound and the molecular weight is within the range of about 2,000 to 15,000;

(B) Alkoxy(EO,PO)a(EO,PO)b—H

wherein the alkoxy group contains 1–20 carbon atoms, EO and PO represent ethylene oxide and propylene oxide, respectively, the weight percent of EO is within the range of 0 to 45% in one of the blocks a, b and within the range of 60 to 100% in the other of the blocks a, b, and the total number of moles of combined EO and PO is in the range of 6 to 125 moles, with 1 to 50 moles in the PO rich block and 5 to 100 moles in the EO rich block;

(C) $RO\text{-}(BO)_n(EO)_x—H$

wherein BO and EO are butoxy and ethoxy respectively, R is C_1 to C_{20} alkyl, n is about 15, and x is about 15;

(D) $HO\text{-}(EO)_x(BO)_n(EO)_y—H$

wherein BO and LO are butoxy and ethoxy, respectively, and n, x and y are each about 15;

(E) $[H(EO)_y(PO)_x]_2N—CH_2—CH_2—N[(PO)_x(EO)_yH]_2$

wherein (EO) and (PO) are ethoxy and propoxy, respectively, the amount of $(PO)_x$ is such as to provide a molecular weight prior to ethoxylation of about 300 to 7500, and the amount of $(EO)_y$ is such as to provide about 20 to 90% of the total weight of said compound;

(F) $HO(C_3H_6O)_x(C_2H_4O)_y(C_3H_6O)_{x'}—H$

having a molecular weight of approximately 4000 with equal parts by weight of ethylene oxide and propylene oxide; and,

(G) $H(EO,PO)_x(PO,EO)_y(EO,PO)_{x'}—OH$

wherein EO and PO are ethylene oxide and propylene oxide, respectively, the group $(PO,EO)_y$ contains 90% PO and has a molecular weight of about 2500, and the groups $(EO,PO)_{x+x'}$ contain about 90% EO and have a molecular weight of about 1700, the minimum ratio of nonionic detergent to quaternary ammonium compound in said composition being not less than 2:1, and in which composition said germicidal quaternary ammonium compound has a phenol coefficient of at least 50 with respect to *S. aureus* and *S. typhosa* at 20° C., and is further characterized by having at least one 8–22 carbon atom containing substituent selected from the group consisting of alkyl and aryl radicals which substituent is joined to the quaternary nitrogen.

2. A germicidal detergent composition as defined in claim 1 wherein the nonionic detergent: quaternary ammonium compound ratio is in the range of about 5:1 to 10:1.

3. A germicidal detergent composition as defined in claim 1 wherein the nonionic detergent is a compound of Formula A.

4. A germicidal detergent composition as defined in claim 1 wherein the nonionic detergent is a compound of Formula B.

5. A germicidal detergent composition as defined in claim 1 wherein the nonionic detergent is a compound of Formula C.

6. A germicidal detergent composition as defined in claim 1 wherein the nonionic detergent is a compound of Formula D.

7. A germicidal detergent composition as defined in claim 1 wherein the nonionic detergent is a compound of Formula E.

8. A germicidal detergent composition as defined in claim 1 wherein the nonionic detergent is a compound of Formula F.

9. A germicidal detergent composition as defined in claim 1 wherein the nonionic detergent is a compound of Formula G.

10. A germicidal detergent composition as defined in claim 1 wherein the nonionic detergent component is a nonionic detergent-iodine complex, the amount of iodine in said complex being about one to two times the amount of said quaternary ammonium compound such as to provide additional germicidal activity.

11. A germicidal detergent composition as defined in claim 1, employing a complex of PVP–I, the amount of iodine in said complex being about one to two times the amount of said quaternary ammonium compound such as to provide additional germicidal activity.

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