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[54] **DETERGENT COMPOSITIONS CONTAINING ENZYME AND CHLORINE SCAVENGER**

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[52] **U.S. Cl.** **252/548;** 252/188; 252/527; 252/529; 252/544; 252/DIG. 11; 252/DIG. 12

[51] **Int. Cl.** **C11d 1/42**

[58] **Field of Search** ..... 252/548, DIG. 12, 544, 252/527, 529

[56] **References Cited**

UNITED STATES PATENTS

3,697,451 10/1972 Mausner 252/548

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[57] **ABSTRACT**

An enzyme composition is provided containing a hydroxyamine chlorine scavenger capable of reacting with residual chlorine in water to form a chloramine compound. The chlorine scavenger prevents enzyme deactivation by residual chlorine. A method of practicing the present invention is also described.

A preferred embodiment of this invention is a detergent composition containing an organic synthetic detergent, an enzyme component, and a hydroxyamine chlorine scavenger capable of reacting with residual chlorine in water to form a chloramine compound. The detergent composition can also contain a builder salt. Among the chlorine scavengers which can be used are tris (hydroxymethyl) aminomethane, 2-amino-2-methyl-1, 3-propanediol, 2-amino-2-ethyl-1, 3-propanediol, 2-amino-1-butanol, 1-amino-2-propanol, 2-amino-1-propanol, and 2-amino-2-methyl-1-propanol.

2 Claims, No Drawings

DETERGENT COMPOSITIONS CONTAINING ENZYME AND CHLORINE SCAVENGER

This is a division of application Ser. No. 76,994 filed Sept. 30, 1970, now U.S. Pat. No. 3755,085.

FIELD OF INVENTION

This invention relates to enzyme compositions which are intended to be used in water which may contain residual chlorine such as is present in municipal water supplies as a result of ordinary sewage treatment processes. One useful application of the invention is in the area of enzyme-containing detergent compositions which are widely used for washing soiled laundry.

BACKGROUND OF INVENTION AND PROBLEMS CONNECTED THEREWITH

Enzymes are organic catalytically-active protein materials which in very low amounts speed up certain chemical reactions. One of their known functions is to break down various types of organic matter (carbohydrates, fats, proteins) into simpler particles, e.g., enzymes that are found in the human digestive system break down food materials into smaller, more assimilable forms. When used in detergent compositions, the enzymes function to break down soils and stains into simpler forms so they can be more easily removed by other detergent ingredients and the washing action.

Enzymes are complex molecules and are subject to attack and deactivation by many different conditions which prevail depending upon the different applications of the enzymes. For instance, incompatibility of enzymes and detergent ingredients such as chlorine bleaching agents is recognized; for example, an article published in Detergent Age, September, 1968, by Dr. Howard E. Worne, titled "The Role of Enzymes in Detergent Compositions" states:

> "Bleaching agents such as perborates, peroxides, or compounds containing active chlorine, strongly inhibit the reaction of proteolytic enzymes, and as such, they must be eliminated from all proposed formulations."

For this reason, care is exercised in formulating detergent compositions in which an enzyme component is contemplated. U.S. Pat. No. 3,451,935 discusses some highly useful ways of overcoming the problems encountered. While this latter discovery has advanced the art materially and has provided, for the first time, large scale production of genuinely effective granular enzyme-containing detergent compositions, it has more recently been discovered that additional problems are encountered in actual usage situations.

Further evaluations have shown that the full potential benefit of enzymatic activity in detergent compositions has not always been enjoyed in practical ordinary household situations. The reason for this has gone unrecognized until the present invention.

It has now been discovered that enzyme activity can be substantially decreased by deactivation of the enzyme component by even small amounts of residual chlorine present in domestic water supply sources. It is this heretofore unappreciated problem that is solved by the present invention.

There are two basic ways of treating waste as part of pollution control in the United States. They are referred to generally as primary and secondary treatments. In a primary treatment, solids are allowed to settle and are removed from the water. The secondary

treatment method used biological processes. A common step in both of these treatment methods involves the addition to the water of varying amounts of free available chlorine as gaseous chlorine or hypochlorites. A major purpose for the chlorine addition is to kill disease producing bacteria, although it also helps to reduce odors.

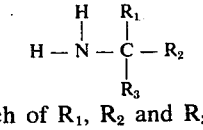
While a portion of the added chlorine escapes from the water during the treatment and handling steps, it has been found that a portion of residual chlorine remains in municipal water supplies. This residual chlorine is sufficient to substantially deactivate an enzyme when it is added to such water.

A major object of this invention is to provide significantly improved benefits in the area of cleaning and laundry performance results obtained with enzyme-containing detergent compositions. While detergent compositions and washing processes represent preferred embodiments of this invention, it, in fact, finds wider application. The invention can be applied broadly to all enzyme usages in water which contains residual chlorine.

SUMMARY OF THE INVENTION AND PREFERRED EMBODIMENTS

It has now been discovered that the deactivation of an enzyme by residual chlorine in water can be prevented by using the enzyme in combination with a hydroxyamine chlorine scavenger which is capable of reacting with the residual chlorine to form chloramines.

The hydroxyamine chlorine scavenger of the present invention has the following formula:



wherein each of R_1, R_2 and R_3 is selected from the group consisting of hydrogen, and alkyl or hydroxyalkyl groups having from 1 to 6 carbon atoms. The alkyl groups can be straight chain or branch chain and the hydroxy can be present on any of the carbon atoms.

The following compounds are illustrative of those which can be used in practicing the present invention:

methylamine,
ethylamine,
1-propylamine,
1-butylamine,
1-pentylamine,
3-amino-1-propanol,
1-amino-2-propanol,
1-amino-2-butanol,
1-amino-3-butanol,
1-amino-4-butanol,
1-amino-2-pentanol,
1-amino-3-pentanol,
1-amino-4-hydroxypentane,
1-amino-5-hydroxypentane,
2-amino-2-methyl-1-propanol,
2-amino-2-methyl-1-butanol,
2-amino-2-methyl-1-pentanol,
2-amino-2-methyl-1-hexanol,
2-amino-2-methyl-1,3-butanediol,
2-amino-2-methyl-1,4-butanediol,
2-amino-2-methyl-1,3-pentanediol,
2-amino-2-methyl-1,4-pentanediol,
2-amino-2-methyl-1,5-pentanediol,

2-amino-2-methyl-1,3-hexanediol,
2-amino-2-methyl-1,4-hexanediol,
2-amino-2-methyl-1,5-hexanediol,
2-amino-2-methyl-1,6-hexanediol.
2-amino-1,3-propanediol,
2-amino-2-methyl-1,3-propanediol,
2-amino-2-hydroxymethyl-1-butanol,
2-amino-2-hydroxymethyl-1-pentanol,
2-amino-2-hydroxymethyl-1-hexanol,
2-amino-2-hydroxymethyl-1,3-propanediol,
2-amino-2-hydroxymethyl-1,4-butanediol,
2-amino-2-hydroxymethyl-1,3-butanediol,
2-amino-2-hydroxymethyl-1,2-pentanediol,
2-amino-2-hydroxymethyl-1,4-pentanediol,
2-amino-2-hydroxymethyl-1,5-pentanediol,
2-amino-2-hydroxymethyl-1,3-hexanediol,
2-amino-2-hydroxymethyl-1,4-hexanediol,
2-amino-2-hydroxymethyl-1,5-hexanediol,
2-amino-2-hydroxymethyl-1,6-hexanediol,
1-amino-1-ethanol,
2-amino-1-propanol,
2-amino-1-butanol,
2-amino-1-pentanol,
2-amino-1-hexanol,
2-amino-1,4-butanediol,
2-amino-1,3-butanediol,
2-amino-1,3-pentanediol,
2-amino-1,4-pentanediol,

Nitroparaffin	Formaldehyde	Intermediate Aldol Product
CH_3NO_2 + (nitromethane)	$3CH_2O$	CH_2OHCCH_2OH (with NO_2, CH_2OH) (tris(hydroxymethyl)nitromethane)
$CH_3CH_2NO_2$ + (nitroethane)	$2CH_2O$	CH_2OHCCH_2OH (with NO_2, CH_3) (2-nitro-2-methyl-1,3-propanediol)
$CH_3CH_2CH_2NO_2$ + (1-nitropropane)	$2CH_2O$	CH_2OHCCH_2OH (with NO_2, C_2H_5) (2-nitro-2-ethyl-1,3-propanediol)
CH_3CHCH_3 (NO_2) (2-nitropropane)	$1CH_2O$	CH_3CCH_2OH (with NO_2, CH_3) (2-nitro-2-methyl-1-propanol)

After neutralizing the catalyst and stripping off unreacted formaldehyde, the nitroalcohol is next reduced over Raney nickel to the corresponding amine. Carbon dioxide is added to the hydrogen stream in the reduction process to neutralize the amine as it is formed. This prevents side reactions which would otherwise occur between the amine and the nitroalcohol.

Aminohydroxy compounds which are representative of the type which are useful in the present invention are further described below:

Physical Properties	2-amino-1-butanol (NH_2)	2-amino-2-methyl-1-propanol (NH_2)	2-amino-2-methyl-1,3-propanediol (NH_2)	2-amino-2-ethyl-1,3,propanediol (NH_2)	tris-(hydroxymethyl)-aminomethane (NH_2)
Formula	$CH_3CH_2CHCH_2OH$	CH_3CCH_2OH (CH_3)	CH_2OHCCH_2OH (CH_3)	CH_2OHCCH_2OH (C_2H_5)	CH_2OHCCH_2OH (CH_2OH)
Molecular Weight	89.14	89.14	105.14	119.17	121.14
Boiling Point, °C	178^{760mm}	165^{760mm}	151 to 152^{10mm}	152 to 153^{10mm}	219 to 220^{10mm}
Melting Point, °C	−2	30–31	109–111	37.5–38.5	171–172
Specific Gravity at 20/20°C	0.944	—	—	—	—
pH of 0.1M Aqueous Solution at 20°C	11.1	11.3	10.8	10.8	10.4
Solubility in Water at 20°C., g/100 ml	Completely Miscible	Completely Miscible	250	Completely Miscible	80

2-amino-1,5-pentanediol,
2-amino-1,3-hexanediol,
2-amino-1,4-hexanediol,
2-amino-1,5-hexanediol,
2-amino-1,6-hexanediol,

The hydroxyamines of the present invention can be prepared by many different syntheses. One satisfactory general method involves reacting a nitroparaffin with formaldehyde in the presence of a caustic catalyst to yield a nitroalcohol. This reaction is a condensation of the aldol type in which one, two or three of the hydrogen atoms attached to the carbon atom holding the nitro group may add to the oxygen of the formaldehyde with the formation of hydroxy methyl-substituted nitroparaffins.

The following equations illustrate the general application of this type of a reaction:

Further suitable synthesis procedures are found in the following patents and technical literature references: U.S. Pat. Nos. 2,755,304 granted July 17, 1956, and 2,946,793 granted July 26, 1960; Japanese Pat. No. 1,235, dated Feb. 24, 1955; Preparation of amino alcohols found in comp. rend. congr. sci. savantes Paris et depts., Sect. sci. 1955, 89-93; Great Britain Patents 764,183 published Dec. 19, 1956; 758,941 published Oct. 10, 1956; 760,215 published October 31, 1956; 8-39,317 published June 29, 1960; Preparation of β-amino alcohols described by J. H. Hunt and D. McHale (Allen & Hanburys, Ltd., Herts, Engl.) J. Chem. Soc. 1957, 2073-7; West Germany Pat. No. 1,096,917 published Jan. 12, 1961.

The invention can be practiced according to several embodiments. Preferably, an enzyme composition is prepared embodying the invention. Such a composition comprises a mixture of an enzyme (either a pure enzyme or an ordinary enzyme preparation consisting of a powder mixture of an active enzyme ingredient and inert salts which are ordinarily found in commercial en-

zyme preparations such as, for example, sodium and calcium sulfates) and a hydroxyamine chlorine scavenger of the type specified above. The amount of each ingredient depends on the use of the composition. For maximum benefits, there should be an amount of hydroxyamine chlorine scavenger sufficient to overcome the residual chlorine. For any given purpose, the amount of aminohydroxy compound required is readily determined by the degree of chlorine protection desired. As a guide to this usage, it has been determined that mole parity (hydroxyamine per each mole of available chlorine) substantially overcomes any chlorine deactivation of the enzyme. This has been shown by demonstrations which reveal that when the hydroxyamine level in a detergent product corresponds on a mole parity basis to the chlorine in wash water, enzyme stain removal performance is comparable to a hydroxyamine-free enzyme product in chlorinefree wash water.

Another important aspect of the present invention is the totally unexpected discovery that when the amount of hydroxyamine chlorine scavenger in a detergent product exceeds the amount of residual chlorine in wash water (on a molar basis), the enzyme stain-removal cleaning performance is significantly greater than the cleaning achieved by a hydroxyamine-free enzyme product in chlorine-free water. This unique performance advantage is not completely understood. It is postulated, however, to be due to the hydroxy-functionality of the hydroxyamine participating in the enzyme catalyzed stain-removal reaction.

As an alternative embodiment to preparing a mixture of an enzyme and a hydroxyamine chlorine scavenger of this invention, the benefits of this invention also can be obtained by following a procedure in which an effective amount of a hydroxyamine chlorine scavenger is added to water containing residual chlorine and in another step adding the enzyme composition, e.g., as an enzyme containing detergent composition.

The present invention finds application with all types of enzymes which are inactivated by chlorine in water including proteases, lipases, amylases, carbohydrases, esterases, and many others. A description of the types of enzymes which can be protected by practice of the present invention appears in U.S. Pat. No. 3,451,935, beginning at Column 6, line 1, and extending to Column 9, line 28. This disclosure is incorporated herein by reference. The preferred enzymes for use in practicing this invention, especially for the detergent composition embodiments, are proteases, lipases and amylases (alpha and beta).

This invention finds special application and provided excellent unexpected improvements in the area of detergency and especially household laundry compositions.

The invention can be practiced by preparing compositions containing only an enzyme preparation and an effective amount of a hydroxyamine as described above. Soiled garments which comprise an ordinary household washing load can be treated e.g., soaked and/or washed with such a composition.

a preferred practice is to use such a binary mixture in combination with an organic synthetic detergent to provide a more complete cleaning and laundry composition.

Organic synthetic detergents useful in practicing this preferred embodiment can be selected from the classes of detergents which include anionic, nonionic, zwitterionic, and ampholytic detergents. While a single active detergent provides satisfactory results, mixed active systems can likewise be used.

The organic synthetic detergents which can be used in practicing the present invention are described in U.S. Pat. No. 3,451,935 beginning at Column 9, line 29, and extending to Column 11, line 59. This disclosure is hereby incorporated herein by reference. The preferred detergents are the anionic class including specifically soap and non-soap anionic detergents such as sodium alkyl benzene sulfonates, the alkyl group being linear or branch and having 10 to 18 carbon atoms, preferably 12 to 16; sodium and potassium alkyl sulfates, the alkyl group having 10 to 18 carbon atoms, e.g., sodium coconut and tallow alkyl sulfate, sodium salt of a condensation reaction product of tallow or coconut alcohol with 1 to 20 ethylene oxide groups, preferably 2to 12 ethylene oxide groups, such as sodium tallow alkylethoxylate averaging three moles of ethylene oxide per mole of tallow alcohol; sodium olefin sulfonates in which the olefin has 10 to 18 carbon atoms, e.g., sodium dodecene sulfonates, sodium hexadecene sulfonates, and mixtures of the anionic detergents.

An unbuilt detergent composition of the present invention comprises from 1 to 99 percent of an organic synthetic detergent, from 1 to 99 percent of an enzyme, and an effective amount of a hydroxyamine chlorine scavenger of the type described above. An effective amount can range from 0.001 to 5 percent by weight of the composition, preferably from 0.005 to 2 percent by weight.

For heavy-duty laundering applications, a preferred embodiment of this invention is a detergent composition which comprises from 0.001 to 10 percent of an enzyme, from 0.001 to 5 percent of an hydroxyamine chlorine scavenger of the type described above and from about 1 to 99.998 percent of a mixture of an organic synthetic detergent and a detergency builder salt, the ratio by weight of said detergent to said builder being in the range of 10:1 to 1:20, and preferably from 5:1 to 1:10. Such a composition provides a pH in aqueous solution in the range of 7 to 12; optimum results are obtained in a pH range of 8 – 11.5.

The detergency builder component can be an inorganic or organic alkaline builder of the type described below.

Examples of suitable water-soluble, inorganic alkaline detergency builder salts are alkali metal carbonates, borates, phosphates, polyphosphates, bicarbonates, silicates and sulfates. Specific examples of such salts are sodium and potassium tetraborates, perborates, bicarbonates, carbonates, tripolyphosphates, pyrophosphates, orthophosphates and hexmetaphosphates. Sodium sulfate, although not classed as an alkaline builder salt, is included in this category.

Examples of suitable organic alkaline detergency builder salts are: Water-soluble aminopolycarboxylates, e.g., sodium and potassium ethylenediaminetetraacetates, nitrilotriacetates and N-(2-hydroxyethyl)-nitrilodiacetates; water-soluble salts of phytic acid, e.g., sodium and potassium phytates -- See U.S. Pat. No. 2,739,942; water-soluble, polyphosphonates, including specifically, sodium, potassium and lithium salts of ethane-1-hydroxy-1,1-diphosphonic acid, sodium, potassium and lithium salts of methylene diphosphonic acid, sodium, potassium and lithium salts of ethylene diphosphonic acid, and sodium, potassium and lithium salts of

ethane-1,1,2-triphosphonic acid. Other examples include the alkali metal salts of ethane-2-carboxy-1,1-diphosphonic acid, hydroxymethanediphosphonic acid, carbonyldiphosphonic acid, ethane-1-hydroxy-1,1,2-triphosphonic acid, ethane-2-hydroxy-1,1,2-triphosphonic acid, propane-1,1,3,3-tetraphosphonic acid, propane-1,1,2,3-tetraphosphonic acid, and propane-1,2,2,3-tetraphosphonic acid; water-soluble salts of polycarboxylate polymers and copolymers as described in U.S. Pat. No. 3,308,067. Specific examples are polymers of itaconic acid, aconitic acid, maleic acid, mesaconic acid, fumaric acid, methylene malonic acid, and citraconic acid and copolymers with themselves and other compatible monomers such as ethylene.

Mixtures of organic and/or inorganic builders described above can be used and are generally desirable. One such mixture of builders is disclosed in U.S. Pat. No. 3,392,121, e.g., ternary mixtures of sodium tripolyphosphate, sodium nitrilotriacetate and trisodium ethane-1-hydroxy-1,1-diphosphonate.

In these heavy-duty formulations, the detergent can be either a single active detergent or a mixture thereof. Similarly, the builder can be a single builder or a mixture of two or more builders.

The present invention can be effectively used in water having a pH in the range of 4 to 12 depending upon the specific ingredients employed. Builerless systems are effective in slightly acid to neutral soaking and washing systems. The built compositions, however, provide optimum cleaning performance results in an alkali pH range, i.e., 7 to 12 and preferably 8 to 11.5.

The following examples serve to demonstrate the present invention. They illustrate the unexpected performance benefits made possible by using a hydroxyamine chlorine scavenger in combination with an enzyme composition whereby the problem os enzyme deactivation in chlorinated wash water is substantially eliminated.

In the following examples, the enzyme preparation consisted of a mixture of 3.42 percent by weight Bacillus subtilis Carlsburg protease (1.5 Anson units), 2.28 percent by weight BPN′ protease (1.5 Anson units). The enzyme preparation also had 7500 α-amylase activity units per gram of said preparation. In the following examples, the enzyme-containing benchmark product was prepared by adding 3.6 parts of the foregoing enzyme preparation to 96.4 parts (all by weight) of the spraydried benchmark product.

EXAMPLE I

Cotton muslin swatches (each 5½ inch square) stained with licorice, gravy, and spinach were washed in 1.5 gallon automatic minature washers (AMW) at three temperatures. Previously unwashed stained swatches were used for each temperature. Four washers were employed (AMW Nos. 1, 2, 3, and 4).

The stained muslin swatches were prepared by passing strips of muslin through a padding bath containing a staining solution, passing the muslin through a two-roll wringer and then drying the stained muslin strips. In order to effect deeper stains, the muslin strips were passed through the staining bath a second time followed by drying over night at 120°F. The strip of muslin was then cut into swatches approximately 5½ inches square in size.

The wash load in each AMW consisted of three swatches of each different stain plus two 12 inch square unstained (total 10 items), white terrycloths. The terrycloths provide bulk for the wash load and promote more precise stain removal data by providing more even agitation. The even agitation is desired because it minimizes the tendency for the swatches to intertwine, twist, or curl.

A series of washes was conducted demonstrating the invention using 75°F. water, 100°F. water and 120°F. water. These are nominal temperatures. The actual temperatures were slightly lower because the water cooled slightly during the procedures.

The benchmark product used in these demonstrations was a spray dried built detergent composition having the following ingredients by weight:

	Weight %
Sodium linear alkyl benzene sulfonate (alkyl group having an average 13.0 carbons)	12.6
Sodium tripolyphosphate	41.5
Sodium nitrilotriacetate	9.6
Sodium silicate (1.6 R)	7.0
Water	10.0
Sodium sulfate	14.0
Enzyme preparation as described above*	.2
Carboxymethylcellulose	.2
Miscellaneous (including brighteners, perfume)	Balance to 100%

Additional conditions in each washer are given in Table I below.

TABLE I

Washing Conditions	*AMW NO. 1	AMW NO. 2	AMW NO. 3	AMW NO. 4
Chlorine concentration (ppm)	0.0	0.0	1.5	1.5
Percent (%) enzyme added to Benchmark product	0.0	0.2	0.2	0.2
Benchmark detergent product usage (g)	6.8	6.8	6.8	6.8
Hydroxyamine chlorine scavenger added to the benchmark detergent product	0.0	0.0	0.0	0.5

*Automatic miniature washer

Table I indicates that the conditions which prevailed in AMW No. 1 were no enzyme, no chlorine, and no chlorine scavenger. Essentially this provided results using just the benchmark detergent product shown above.

The conditions in AMW No. 2 differed from AMW No. 1 in the addition to the benchmark detergent product of 0.2% of an enzyme ingredient.

The conditions in AMW No. 3 differed from AMW No. 2 in the presence of 1.5 ppm concentration of chlorine in the wash water.

The conditions in AHW No. 4 differed from AMW No. 3 in the addition to the benchmark detergent product of 0.5 parts of a hydroxyamine chlorine scavenger which was tris(hydroxymethyl)amino methane (TRIS).

These varied conditions provided an opportunity to demonstrate the present invention with meaningful comparisons.

The washing procedure consisted of the following steps:

Step 1. The automatic miniature washers (AMW) were filled to their 1.5 gallon capacities with water of the desired washing temperature.

Step 2. The water hardness was adjusted to 7 gr./gal. by adding 5.5 ml. of a solution which is 7570 gr./cc. hardness (3 pts. Ca/1 pt. Mg. - both expressed as $CaCO_3$). Hardness contribution from the load was neglected.

Step 3. The chlorine concentration of each washer was adjusted. To provide for a demonstration for comparative purposes of 0.0 ppm Cl_2, 1 ml. of a 0.1N $Na_2S_2O_3$ solution was added to the washer. To achieve 1.5 ppm Cl_2, 3.9 ml. of a chlorine solution (made from adding 3 parts water to 1 part of an aqueous solution containing 0.4% Cl_2) was added to the washer.

Step 4. The product being demonstrated was added to the washer, and the water was agitated for two minutes. The product in AMW No. 4 (see Table I above) was made by adding 0.5 parts of 99+% pure TRIS chlorine scavenger to 99.5 parts of the above identified benchmark product.

Step 5. After this two-minute agitation, the stain swatches were added. The load was washed for 10 minutes followed in order by a spin, a rinse, and another spin to damp dry.

Step 6. Each load was tumbled to dryness in a steam dryer operating at 160°F. maximum.

Step 7. Each swatch (except the spinach) was ironed. The spinach swatches were smooth out by hand.

Step 8. Hunter Whiteness grades were obtained for each swatch from a Hunter Color Difference Meter. This instrument is designed to distinguish color differences and operates on the tristimulus colorimeter principle wherein the 45° diffuse reflectance of an incident light beam on a test specimen is measured through a combination of green, blue and amber filters. The electrical circuitry of the instrument is so designed that lightness and chromaticity values for the test specimen are read directly. The department from white (MgO being taken as a standard white) of the test specimen is calculated by introducing the lightness and chromaticity values so obtained into a complex formula supplied by the manufacturer. An evaluation of relative whiteness performance compared to a standard detergent composition is thus obtained for the test formulations. These are later compared with other values obtained from other test samples.

A more comprehensive description of this instrument and its mode of operation appears in Color in Business, Science and Industry, by Deane B. Judd, pages 260–262; published by John Wiley & Sons, New York (1952).

The results are shown in Table II. The product used in AMW No. 1 without enzyme in 0.0 ppm. Cl_2 serves as the benchmark for measuring the effectiveness of the present invention as illustrated in AMW No. 4. The least significant difference at α=0.05, (LSD_{05}), is shown for each stain in each treatment in Table II.

The first column, (AMW No. 2-AMW No. 1), shows the degree of improvement in whiteness cleaning, in terms of Hunter Units, when an enzyme ingredient is used with the benchmark product in 0.0 ppm Cl_2.

The second column, (AMW No. 3-AMW No. 1), illustrates the deterioration in performance when the benchmark product with an enzyme ingredient is used in chlorinated wash water. All Δ W values less than LSD_{05} (column 5) indicate no significant performance advantage for the E-base in chlorinated water. Each of the values in the second column (AMW No. 3-AMW No. 1) is of this magnitude indicating that the chlorine has destroyed the enzyme and substantially eliminated enzymatic activity. Essentially, the product with enzyme used in chlorinated wash water, i.e., the product used in AMW No. 3, performs the same as the benchmark product, i.e., the product used in AMW No. 1, which contained no enzyme at all used in chlorine-free wash water.

The third column, (AMW No. 4-AMW No. 1), illustrates the effectiveness of the chlorine scavenger tris(hydroxymethyl)aminomethane, referred to at times in this specification as TRIS. It is notable that, in each case, cleaning due to enzyme activity in chlorinated water was not only restored but actually increased to levels greater than enzyme cleaning performance in non-chlorinated water. These results indicate that the detergent compositions of this invention are synergetic detergent compositions providing an unexpectedly superior level of cleaning. These synergetic results are obtained even with wash waters having temperatures ranging from cool water to hot water. This is evidenced with the spinach, gravy, and licorice stains demonstrated in Table II.

TABLE II

Chlorine-deactivation by tris(hydroxymethyl)aminomethane

T=75° F.	Δ W* **(AMW NO. 2-AMW NO. 1)	(AMW NO. 3-AMW NO. 1)	(AMW NO. 4-AMW NO. 1)	LSD
Spinach	5.2	−1.5	8.2	3.1
Gravy	5.1	0.8	6.1	1.1
Licorice	1.2	−0.5	3.4	1.1
T=100°F.				
Spinach	11.9	−0.6	16.3	2.9
Gravy	6.3	0.0	9.2	1.5
Licorice	3.3	0.7	4.6	1.0
T=120°F.				
Spinach	15.1	−0.4	17.6	4.2
Gravy	9.7	−0.5	11.8	1.1
Licorice	5.4	−0.7	6.2	1.1

*The Δ W values are the difference between the first and second washers identified in each column.

	Additives	Chlorine Level in Wash Water
**AMW NO. 1:Used benchmark product	0.0% E-base 0.0% TRIS	0.0 ppm Cl_2
AMW NO. 2:Used benchmark product	+0.20% E-base+0.0% TRIS	0.0 ppm Cl_2
AMW NO. 3:Used benchmark product	+0.20% E-base+0.0% TRIS	+ 1.5 ppm Cl_2
AMW NO. 4:Used benchmark product	+0.20% E-base+0.5% TRIS	+ 1.5 ppm Cl_2

EXAMPLES II - V

The procedures described in Example I above were repeated with other illustrative aminohydroxy chlorine scavenger compounds at 75° and 125°F. washing temperatures. The aminohydroxy compounds were used at the same level as Example I (i.e., 0.5 parts aminohydroxy scavenger added to 99.5 parts benchmark product. The results are shown in Table III. Here Δ W values represent the difference in Hunter Whiteness Units between values obtained with the benchmark product with an enzyme and a chlorine scavenger and the benchmark product with an enzyme but without a protective chlorine scavenger (both operating in 1.5 ppm Cl_2 wash water).

The 2-amino-2-methyl-1,3-propanediol (AMPD) and the 2-amino-2-ethyl-1,3-propanediol (AEPD) exhibit comparable chlorine scavenging effectiveness for all three stains at both temperatures, i.e., 75°F. and 125°F. The 2-amino-1-butanol and 1-amino-2-propanol exhibit maximum chlorine scavenging effectiveness at 125°F.

TABLE III

T=75° F.	Example I 2-amino-2-methyl-1,3-propanediol ΔW	Example III 2-amino-2-ethyl-1,3-propanediol	Example IV 2-amino-1-butanol	Example V 1-amino-2-propanol
Spinach	5.9	2.4	−0.2	−2.6
Gravy	6.0	4.7	−0.8	−1.2
Licorice	1.2	3.8	−0.3	−0.5
T=125° F.				
Spinach	10.4	14.9	3.7	4.1
Gravy	12.1	13.9	4.3	3.9
Licorice	1.9	4.0	−0.8	0.4

EXAMPLE VI

Results similar to those achieved in Example I are obtained when the following hydroxyamine chlorine scavengers are substituted in whole or in part for the TRIS scavenger in Example I: methylamine, 1-pentylamine, 3-amino-2-propanol, 1-amino-4-hydroxypentane, 2-amino-2-methyl-1-butanol, 2-amino-1,3-propanediol; 2-amino-2-hydroxymethyl-1,6-hexanediol, 1-amino-1-lethanol, 2-amino-1,4-hexanediol.

EXAMPLE VII

A synergetic detergent composition of the present invention comprises:

Sodium dodecyl benzene sulfonate (dodecyl being linear)	20
Sodium tripolyphosphate	50
Sodium silicate (1.6 R)	10
Sodium sulfate	15
Water	4.4
Alcalase proteolytic enzyme	.3
Tris(hydroxymethyl)aminomethane chlorine scavenger	

This composition is effective in wash water containing up to 10 ppm chlorine. When this composition is used under washing conditions in which the molar concentration of chlorine scavenger exceeds that of the residual chlorine an unexpectedly superior stain removal is achieved.

EXAMPLE VIII

When the following hydroxyamine compounds are substituted wholly or partially for the TRIS of Example VII, substantially similar results are achieved: 2-amino-2-methyl-1,3-propanediol; 2-amino-2-ethyl-1,3-propanediol; 2-amino-1-butanol; 1-amino-2propanol.

Whereas the preceding examples illustrate the composition embodiments of the present invention, it is to be noted that the hydroxyamine chlorine scavengers can just as effectively be added in an effective amount to the chlorinecontaining wash water in a separate step prior to a washing step.

In this manner, the residual chlorine is reacted with the hydroxyamine chlorine scavenger and is thus not available to attack and deactivate an enzyme ingredient which is added to the water such as an enzyme-containing laundry detergent composition.

EXAMPLE IX

Wash water containing 3.5 ppm residual chlorine and having a temperature of 120°F. is provided. A chlorine scavenger compound which is tris(hydroxymethyl-)aminomethane is added to the wash water in an amount of 6 ppm. This amount corresponds to molar parity between the scavenger and the chlorine. Soiled and stained garments are added to the wash water and laundered therein using the benchmark composition described in Example I. Superior stain removing performance results are obtained as compared to this process in which the chlorine scavenger is omitted.

EXAMPLE X

In Example IX, synergetic cleaning results are obtained when the amount of tris(hydroxymethyl) is increased to 12 ppm.

EXAMPLE XI

A soaking detergent composition providing synergetic stain removing properties comprises:

Sodium linear dodecyl benzene sulfonate	99%
Alcalase protease enzyme	.5%
Tris(hydroxymethyl)aminomethane	.5%

EXAMPLE XII

In Example XI, substantially the same results are obtained when the sodium linear dodecyl benzene sulfonate is replaced with sodium tallow alkyl sulfate, sodium coconut alkyl sulfate, sodium C_{12-20} olefin sulfonate, or a condensation product of one mole of coconut alcohol and 6 moles of ethylene oxide.

We claim:

1. A detergent composition comprising from about 1 – 99 percent by weight of an organic synthetic detergent, from about 1 – 99 percent by weight of an enzyme, and from about 0.001 – 5 percent by weight of a chlorine scavenger selected from the group consisting of tris(hydroxymethyl)-aminomethane, 2-amino-2-methyl-1,3-propanediol; 2-amino-2-ethyl-1,3-propanediol; 2-amino-1-butanol; 1-amino-2-propanol; 2-amino-1-propanol; and 2-amino-2-methyl-1-propanol.

2. A detergent composition according to claim 1 wherein said enzyme is a protease enzyme and said chlorine scavenger is tris-(hydroxymethyl)-aminomethane.

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