

## UNITED STATES PATENT OFFICE

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GERMICIDALLY ACTIVE DEIONIZING  
AGENTS FOR ALKALINE pH SOLUTIONS

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5 Claims. (Cl. 260—482)

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This invention relates to laundering operations wherein soiled clothes are agitated in hot aqueous alkaline pH solutions containing water soluble alkali metal-fatty acid soap compounds to free the soiling dirt from the clothes and to suspend the dirt in the aqueous solution followed by draining off the major portion of the dirty soap solution and rinsing one or more times in clear water to remove the remaining dirty soap solution from the washed clothes.

In such general process, as the remaining dirty soap solution is diluted with water during the first rinsing step, the dirt particles suspended in the soap solution tend to re-precipitate upon the clean clothes along with insoluble metal soap compounds formed by reaction of the alkali metal soap compounds with the soluble salts present in the rinse water and metal hydroxides precipitated in such alkaline pH solutions. This reaction imparts a grey tinge to the clean clothes which subsequently must be removed by "blueing" and "souring" rinses, common in the art.

In addition, commercial laundry practice requires the use of disinfectants and bactericidal agents to prevent the spread of disease in laundry, obtained from a plurality of sources, washed in the same soap solutions.

The object of the present invention is to provide a germicidally active-deionizing agent for use in the laundering of clothes, particularly during the rinse removal of remaining dirty soap solutions from the clothes.

Another object is to facilitate the laundering of clothes by the use of a germicidally active-deionizing rinsing agent inhibiting the precipitation of dirt, insoluble soap compounds and metal oxides upon the clothes during the washing and rinsing operations and eliminating thereby the necessity of subsequently treating the clothes to remove same or to overcome the effect of same and to sterilize the said clothes.

A further object is to provide a germicidally active-water deionizing agent for use in alkaline pH solutions and in the presence of alkali metal soap compounds.

Still another object is to provide a germicidally active detergent consisting of a mixture of water soluble soap compounds and a germicidal quaternary ammonium compound.

Other objects will be apparent as the invention is more fully hereinafter disclosed.

In accordance with these objects I have discovered that the mono- to tetra-quaternary ammonium salts of ethylene diamine tetraacetic acid are strong germicidally active compounds

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soluble in alkaline pH solutions and stable in said solutions in the presence of alkali metal-fatty acid soap compounds.

I have further discovered that the mono-quaternary ammonium salt of ethylene diamine tetraacetic acid after neutralizing the remaining carboxylic acid groups with caustic alkali is, in addition to being germicidally active, a strong deionizing agent in aqueous solutions functioning to remove from such aqueous solutions metal ions tending to precipitate insoluble soap compounds and to solubilize such basic metal ions precipitable in such alkaline pH solutions as basic oxides, hydroxides and carbonates.

Further, I have discovered that the mono-quaternary ammonium salt of ethylene diamine tetraacetic acid in which the primary carboxylic group of the second amino group has been esterified by reaction with a mono or poly alcohol and the two remaining secondary carboxylic groups have been neutralized by caustic alkali is, in addition to being germicidally active, a more powerful deionizing agent and precipitate-solubilizing agent than the mono-quaternary ammonium-tri-alkali metal salt of ethylene diamine tetraacetic acid.

Furthermore, I have discovered that these quaternary ammonium compounds are compatible in all proportions with water soluble soap compounds and that germicidal mixtures thereof may be formed with the quaternary ammonium compound of the mixture also functioning therein as an anti-oxidant.

These discoveries as to the chemical properties of the above identified quaternary ammonium salts of ethylene diamine tetraacetic acid have led me to adapt the same as germicidal-deionizing agents for use in association with water soluble soap compounds, particularly alkali metal-fatty acid soap compounds, and as one specific embodiment thereof I will disclose the invention as it is adapted for utility in the laundering of clothes. Each of the compounds, above identified, are miscible in all proportions with alkali metal-fatty acid soap compounds and are freely soluble in alkaline pH solutions containing alkali metal soap compounds.

The present invention contemplates the incorporation of said quaternary ammonium salts of ethylene diamine tetraacetic acid in soap (bar, powder, flake or liquid) forming thereby a bactericidally active detergent composition having strong deionizing properties, and also contemplates the use of the said quaternary ammonium salts as deionizing and bactericidally active ad-

dition agents to water or to alkaline pH solutions or to such solutions containing alkali metal-fatty acid soap compounds, such as during the rinsing of the washed clothes to free the clothes of remaining dirty soap solutions.

As a specific embodiment of the invention, but not by way of limitation, I will describe the same as it has been adapted to use in standard laundry practice in the case of a specific quaternary ammonium compound known in the art under the trade name "Safran" and chemically as dimethyl benzyl lauryl ammonium chloride. This particular quaternary ammonium compound has heretofore in the art been recognized as a strong antiseptic and bactericidal agent. In alkaline pH solutions and in aqueous solutions of alkali metal-fatty acid soap compounds, however, the compound is known to be inactivated and precipitated, respectively.

The mono-quaternary ammonium salt of ethylene diamine tetraacetic acid is preferably formed from this specific quaternary ammonium compound by reacting the quaternary ammonium hydroxide with the amino acid. The amino acid is insoluble in water but dissolves readily in an aqueous solution of the quaternary ammonium hydroxide. The mono-quaternary ammonium salt is formed by dissolving one molar weight of the amino acid in an aqueous solution containing one molar weight of the quaternary ammonium hydroxide. The amount of water present in the solution may be widely varied without essential departure from the invention.

The resulting aqueous solution of the mono-quaternary ammonium salt of ethylene diamine tetraacetic acid is neutralized with 3 molar weights of caustic alkali (NaOH) and the resultant mono-quaternary ammonium-tri-alkali metal salt of ethylene diamine tetraacetic acid is recovered from the aqueous solution by evaporating off the water of solution.

The white dry-powder salt recovered may be added to the alkaline pH soap solution used in washing the dirty clothes or may be incorporated in the soap detergent employed in forming said soap solution, as may be desired.

I have found it preferable to incorporate from a small percent up to 10% of the quaternary ammonium-tri-alkali metal salt of ethylene diamine tetraacetic acid in the soap detergent before the addition of the soap to the washing solution. Alternatively, the same effect is produced by adding from a small percent up to 10% (by weight of the soap detergent added) of the quaternary ammonium-tri-alkali metal salt to the water used in forming the soap solution prior to the addition of the soap compounds thereto.

The incorporation of the quaternary ammonium salt in the soap detergent or the addition of the quaternary ammonium salt to the water prior to the addition of the soap compounds thereto, insures against the precipitation of insoluble soap compounds by reaction of the soap compounds with hardening constituents present in the water and prevents the precipitation of insoluble metal oxides and hydroxides in the alkaline pH washing solution thus formed.

The reaction by which the precipitation of insoluble soap compounds and insoluble metal oxides and hydroxides is inhibited by the quaternary ammonium salt is quite complex and difficult to represent by chemical equations. In general, ethylene diamine tetraacetic acid, is a strong chelate-forming compound in aqueous solution and this chemical property is believed

to be the major chemical property which stabilizes the present salt in aqueous solution under the widely varied conditions of temperature, concentration of salt, amount and kind of water-hardening constituents present, etc., normally encountered in laundry operations. Suffice it to say, however, that the quaternary ammonium salt is extremely stable in alkaline pH solutions as the quaternary ammonium ion is not displaceable by the lesser basic alkali metal or other positive metal ions present in the solution under the conditions of extreme dilution of the quaternary ammonium salt in the washing solution or the concentration of sodium ions present therein. However, the complex amino acid negative ion of the compound, in its highly ionized condition or state in the solution, is highly unstable and extremely reactive chemically at the other carboxylic acid groups with all other basic metal ions present in the solution. This chemical activity is believed due to the liberation, upon ionization, of the residual valencies normally present on the pentavalent nitrogen atom of each amino group which residual valencies attract to the nitrogen positive and negative ions present in the solution to stabilize the nitrogen atom in its pentavalent state. While the positive metal ions cannot displace the quaternary ammonium and alkali metal positive ions in the carboxylic groups of the salt, they can and do satisfy the released valencies on the pentavalent nitrogen atoms in the amino acid negative ion. Such complex compounds are with difficulty decomposed by free alkali even at temperatures approximating the boiling point of water in such washing solutions. Many other amino polycarboxylic acids are chelate-forming compounds to a greater or lesser degree and may be substituted in part or in whole for ethylene diamine tetraacetic acid without departure from the present invention, as one skilled in the art will recognize.

The addition of from a small percent as low as 1% up to 10% of this quaternary ammonium-tri-alkali metal salt (based on the weight of the soap compounds added) to the water of the alkaline pH solution, prior to or simultaneously with the addition of the soap compounds thereto completely deionizes water of average hardness and mineral content so that the precipitation of insoluble metallic soap compounds and basic metal compounds is inhibited completely.

Following usual washing operations involving agitation of the dirty clothes in the soap solution to free the soiling dirt from the clothes and to suspend the same in the soap solution, the dirty soap solution is drained off from the washed clothes as heretofore practiced. One or more of the washing operations may be practiced, if desired or deemed necessary, to remove all of the soiling dirt from the clothes.

The washed clothes containing the residual dirty soap solution left from the last or final draining operation are then agitated one or more times in water containing said mono-quaternary ammonium-tri-alkali metal salt of ethylene diamine tetraacetic acid to free the clothes from the residual dirty soap solution. The amount of said salt to be added to the rinse water may vary widely, from a small amount to a large amount depending upon the amount of water hardening constituents present therein and the amount of precipitable metal ions present in the solution. Usually 5 to 10 grams per gallon of water is ample protection in the case of water con-

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taining relatively large amounts of hardening constituents.

With water of not over medium hardness and low iron content, from 2 to 10 grams of the salt per gallon of water used is ample to completely deionize the water and to impart thereto high germicidal activity.

This amount of the salt should be added to each rinse water for best results. After thorough rinsing in at least two rinse waters, the clothes may be wrung dry and hung up to dry as per usual practice without further treatment by blueing or souring or disinfecting as heretofore practiced.

As an alternative and more effective agent to that above described, one of the remaining carboxylic groups of the mono-quaternary ammonium salt, above identified, is first esterified with a mono- or poly-alcohol and the mono-quaternary ammonium-ester then is neutralized with caustic alkali to form a mono-ester, mono-quaternary di-alkali metal salt of ethylene diamine tetraacetic acid. This compound is even more effective as a deionizing agent and germicidal agent in alkaline pH solutions and in alkaline pH solutions containing alkali metal soap compounds than the mono-quaternary tri-alkali metal salt of the above specific embodiment.

To form this salt, one molar reacting weight of a poly-alcohol, such as glycerine, is added to the aqueous solution of the mono-quaternary ammonium salt formed as above described and the solution is heated under a high vacuum to drive off the water present and to complete the esterification reaction. The resulting mono-ester-mono-quaternary ammonium salt product is redissolved in water, the remaining carboxylic acid groups neutralized with caustic alkali and the water of solution is again removed by evaporation to dryness.

This compound is completely miscible in all proportions with soap compounds and is highly soluble in water and is extremely stable in relatively high alkaline pH solutions at temperatures up to the solution boiling point.

In laundry operations this ester compound may be used in about the same proportions as hereinabove specified for the mono-quaternary ammonium-tri-alkali metal salt compound and in the same manner with better and more efficient results both as a germicidal agent and as a deionizing agent.

As a second alternative compound I may employ a mixture consisting of a relatively small amount of the tetra-quaternary ammonium salt of ethylene diamine tetraacetic acid and a large amount of the quaternary ammonium base. Usually 10% to 20% of the salt per unit weight of the mixture gives the best results.

As a third alternative I may employ a mixture consisting of a relatively small amount of the mono-quaternary ammonium salt and a relatively large amount of the tetra sodium salt of ethylene diamine tetraacetic acid. Usually 10% to 30% of the salt per unit weight of the mixture gives the best results.

The mixture of the second alternative above given has unusually strong germicidal properties and exceptionally strong deionizing properties being unusually effective as a deionizing agent for calcium salts. In the presence of large amounts of alkali metal-fatty acid soap compounds, however, some precipitation of insoluble quaternary ammonium-fatty acid soaps may be obtained and the use of this compound generally is restricted

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to rinsing operations in the substantial absence of fatty acid soap compounds.

The mixture of the third alternative, however, is utilizable in the presence of alkali-metal fatty acid soap compounds being a stronger deionizer agent than the mono-quaternary ammonium salt. In water of exceptional hardness this mixture is preferred in the washing and rinsing solutions, the amount used in the rinse water being increased to from 10 to 20 grams per gallon in order to obtain equivalent germicidal activity.

Another mixture offering wide utility in the art is a mixture consisting of the quaternary ammonium compound and the tri-alkali metal salt of ethylene diamine tetraacetic acid containing about 10% to 20% of the tri-alkali metal salt. This mixture appears to be about 3 times as strong a deionizing agent as the tetra-alkali metal salt of ethylene diamine tetraacetic acid and to be extremely stable in high pH solutions in addition to having strong bactericidal properties. The mixture appears compatible in all proportions with alkali metal soap compounds in the dry state or in aqueous solutions, contrary to expectations.

The efficiency of the compounds above described as germicidal agents is difficult to establish due to the great variation of conditions involved in commercial and domestic laundry practices. However, experimental tests have indicated that the quaternary ammonium salts above described are strong bactericidal agents equal to or superior to other bactericidal agents under identical test conditions and the bactericidal activity of the compounds is unaffected by anionic compounds such as alkali metal-fatty acid soap compounds. Many tests on clothes washed and rinsed in the presence of these compounds have shown complete sterility as to bacteria and fungi commonly present in and on such dirty wearing apparel.

It is believed apparent from the above disclosure that any other bactericidally active quaternary ammonium compound may be substituted for "Safran" in the above specific examples given without essential departure from the present invention, such as those known in the art under the trade name "Hyamine 1622" and "Roccal," the composition of which varies somewhat as the positive ion of all such quaternary ammonium compounds are characterized by being strong bactericidal agents and by being stronger bases than alkali metal ions, the two characteristics required of the quaternary ammonium ion in the present invention.

This application is a continuation application of my prior application Serial No. 713,078 filed November 29, 1946, now abandoned.

All such modifications and departures in the invention are contemplated as may fall within the scope of the appended claims.

What I claim is:

1. A bactericidally active deionizing agent for aqueous solutions, said agent consisting of a chemical compound consisting of ethylene diamine tetraacetic acid having at least one of the carboxylic groups neutralized by a basic bactericidally active quaternary ammonium ion and the remaining carboxylic groups neutralized by alkali metal ions.

2. A bactericidally active deionizing agent for aqueous solutions, said agent consisting of a chemical compound consisting of ethylene diamine tetracarboxylic acid having at least one of the carboxylic groups neutralized by a basic

bactericidally active quaternary ammonium ion, another esterified by a glycerine and the remaining carboxylic groups neutralized by alkali metal ions.

3. A bactericidally active deionizing agent for aqueous solutions, said agent consisting of the mono- to tetra-salt of ethylene diamine tetraacetic acid and dimethyl benzyl lauryl ammonium hydroxide.

4. The agent of claim 3, wherein said salt consists of the mono salt and wherein the remaining carboxylic groups of the tetra acid are neutralized by an alkali metal ion.

5. The agent of claim 3, wherein said salt consists of the mono salt of said dimethyl benzyl lauryl ammonium hydroxide and wherein the remaining carboxylic groups of the tetra acid are neutralized by sodium ions.

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# REFERENCES CITED

The following references are of record in the file of this patent:

## UNITED STATES PATENTS

| Number    | Name      | Date           |
|-----------|-----------|----------------|
| 2,302,805 | Schussler | Nov. 24, 1942  |
| 2,317,999 | Leuchs    | May 4, 1943    |
| 2,384,817 | Chitwood  | Sept. 18, 1945 |
| 2,384,818 | Curme     | Sept. 18, 1945 |
| 2,428,353 | Bersworth | Oct. 7, 1947   |

## OTHER REFERENCES

- Buntzinger, "Zeit. Anorg. Chem.," vol. 251, pp. 285-294 (1943).  
 Pfeiffer, "Ber. Deut. Chem.," vol. 76B, pp. 847-855 (1943).  
 Klemm, "Zeit. Anorg. Chem.," vol. 252, pp. 225-226 (1944).