ABSTRACT OF THE DISCLOSURE

A nonionic, substantially non-foaming, hydrolytic detergent composition including a nonionic detergent, a non-foaming carrier, and a minor amount of at least one hydrolytic enzyme.

This invention relates to improved nonionic detergent compositions containing hydrolytic enzymes and to their application in various cleaning operations. Surface-active agents (surfactants) have a molecular structure whereby a highly polar (hydrophilic) function is located at one end of a long non-polar (hydrophobic) hydrocarbon chain. In recent years such surfactants have replaced soap, the sodium salt of a long hydrocarbon chain acid, as the principal commercial and household detergents. These surfactants have proved to be advantageous cleaning agents because of the diametrically opposed properties contained within each molecule which enables the surfactant to alter the surface energy of a solid or liquid. In this manner the cleansing action of a cleaning agent such as water, is enhanced as the surfactant, through its hydrophilic function, reduces the interfacial tension between the water and dirt particles. In addition, the surfactant, because of the hydrophobic function, attracts the dirt particle and assists the aqueous medium in removing the particle from the surface of material being cleaned.

Three types of synthetic detergents are commercially available: (1) anionic, for example, the sodium salts of medium chain-length (7-18 carbon), alkyl sulfates or sulfonates; (2) cationic, such as the tertiaryammonium halide; and (3) non-ionic, including products made from tall oil by reaction with ethylene oxide to form low foaming esters.

The anionic type of synthetic detergents is especially valuable in cleaning operations not only because of the afore-mentioned hydrophilic and hydrophobic functions, but also because metallic ions, which are formed through the introduction of the detergent into an aqueous medium, assist in the saponification of organic compounds such as esters. This combination of properties intensifies the cleaning capability of anionic type surfactants, especially in comparison to the less polar nonionic detergents. However, the highly hydrophilic synthetic detergents have certain undesirable characteristics because of their alkalinity which causes chemical damage to both synthetic and natural plant or animal fibers as well as irritation, drying and scaling of human and animal skin.

It is well known that the nonionic detergents, although possessing little if any of the adverse ancillary effects of anionic detergents, nevertheless, are not as satisfactory in many applications because they are not as strongly hydrophilic nor do they readilyassist in the breakdown of complex organic compounds. Therefore, the nonionic detergents usually do not have the desired cleaning capacity in the applications here concerned.

Broadly, a principal object of this invention is to prepare a nonionic detergent composition of substantially increased cleansing capability, yet without the undesirable side effects contained in detergents of the anionic type. This object is accomplished by providing nonionic detergents in a composition having at least one type of hydrolytic enzyme, for use in removing dirt particles which contain the organic matter found on various contaminated surfaces. It is a further object of this invention to provide an improved detergent composition for either household or commercial application which virtually eliminates the chemical damage to synthetic and natural plant and animal fibers heretofore caused by the strongly hydrophilic cation-type synthetic detergents. It is another object of this invention to provide an improved nonionic detergent composition for either household or commercial application which virtually eliminates irritation, drying and scaling of human and animal skin. It is still a further object of this invention to provide a nonionic synthetic detergent composition having the cleaning characteristics of the more strongly hydrophilic anionic detergents presently available.

A further object of this invention is to provide a cleaning system whereby hydrolytic enzymes in the environment of a nonionic detergent catalyze the hydrolysis of organic matter such as proteins, fats, starches and the like contained in dirt particles. Still another object of this invention is to provide a hydrolytic enzyme-containing nonionic detergent composition which enhances the softening and brightening of synthetic and animal fiber during the cleaning function. It is still a further object of this invention to provide a detergent composition of the type described which may be utilized in a dry or a liquid form. An additional object of this invention is to provide a liquid detergent having high cleaning power yet at a minimum of non-active ingredient content thereby reducing bulk and shipping costs.

Still another object of this invention is to prepare a nonionic detergent composition which is particularly desirable for the cleaning of delicate pieces of wearing apparel.

A still further object of this invention is to provide a nonionic detergent composition which will, when discharged into the drain lines and sewers, assist in the acceleration of the rate of waste decomposition, thereby resulting in a shorter retention time, more satisfactory effluent to discharge run off and in a general increase in the effectiveness of the sewage system. These objects will become more easily understood and other aspects will become more apparent from the following description of the invention.

It has now been found that the chemical properties of commercially available nonionic detergents can be unexpectedly modified so that the resulting detergent has substantially enhanced cleaning capabilities. This has been found to be obtained by combining a small quantity of hydrolytic enzymes with the nonionic detergent composition.

Enzymes—catalysts produced by living cells for the purpose of accelerating the reactions that occur under the conditions existing in living matter—have heretofore been isolated and found to be suitable in limited applications such as to assist in the degradation of fats, starches, proteins and other forms of organic waste material in sewage systems. However, until the present invention, hydrolytic enzymes, i.e., those enzymes which catalyze the hydrolysis of complex organic molecules to simpler, more soluble and degradable compounds, have not been known to have certain other desirable applications. For example, hydrolytic enzymes (hydrodases) such as proteases, including papain, trypsin, chymotrypsin and peptidase; esterases such as lipase and butyrase; carbohydrases such as cellulase, diastase, amylase and lactase have here been
found compatible with nonionic detergents having a pH of about 7, provided that the resulting detergent composition contains no more than about 5% water by weight of the nonionic detergent. When such conditions are maintained in an enzyme-containing detergent composition during storage and prior to consumer use, the catalytic effect of the hydrolytic enzymes is not inhibited and the enzymes present remain active to substantially improve the cleaning capability of the otherwise mild nonionic detergents.

The term "hydrolytic enzymes" as used throughout this specification and the appended claims is meant to include all those enzymes which are known to catalyze the hydrolysis of various types of organic matter. The preparation of such enzymes is well known to those of ordinary skill in the art. For example, U.S. Patent No. 3,031,380, issued Apr. 24, 1962, illustrates a typical process for preparing protease and amylase enzymes.

Although it is not intended for the invention to be limited to any specific theoretical concept, it appears that where a detergent carrier solution is alkaline, as when an anionic detergent is employed, the concentration of hydroxyl ions has a denaturing effect on the enzymes. Furthermore, conventional anionic detergents contain additional components which increase the alkalinity concentration of the catalytic activity of the hydrolytic enzymes with respect to the aforementioned hydrolysis reaction, thereby minimizing and in some cases completely inhibiting catalytic activity. But when the hydrolytic enzymes are maintained in a neutral environment such as that found in a nonionic-type detergent, the enzymes are able to fully perform their catalytic function in the hydrolysis reaction of compounds.

Similarly, large concentrations of water have also been found to have a deteriorating effect on the catalytic activity of hydrolytic enzymes. Extensive experimentation has shown that during storage in water, and in the absence of material capable of being hydrolyzed, the enzymes tend to "digest" themselves. Therefore, where water is either minimized or eliminated from the stored nonionic detergent composition to which hydrolytic enzymes have been added, the resulting enzyme-containing detergents possess heretofore unobtainable cleaning capability. This cleaning power is retained in the liquid storage periods to which commercial detergents are normally subjected. In addition, the minimizing of the water content of the composition produces the advantages of reducing the bulk of the detergent composition to permit substantial savings in shipping and storage costs.

It is intended to include in this invention those compositions which, prior to usage, are maintained either as a dry powder, or as a substantially non-aqueous liquid system. The dry mixture has been found to be especially suitable for application as a rug and upholstery cleaner while the liquid composition displays unique and desirable characteristics in commercial and household laundry applications.

In a liquid environment, the hydrolytic enzymes have been found to maintain their catalytic capacity provided that they are stored in an organic carrier such as glycerine, especially where the glycerine is of high purity, i.e., at least 99%. Small amounts of water may be tolerated to solubilize the enzymes only when a non-aqueous carrier such as glycerine is also present.

In composition according to the present invention it is advantageous to employ the enzymes in an amount sufficient to catalyze the hydrolysis of organic matter contained in dirt particles on a contaminated surface. Useful concentrations include quantities up to about 1% by weight of the total detergent system. Of course, substantially larger amounts may be incorporated where economics is not an important consideration; but where cost is a factor use of less than about 1%, i.e., from about 0.05 to about 0.1% of hydrolytic enzymes by weight of the total detergent composition is preferable.

The nonionic detergents suitable for the purposes disclosed herein are readily commercially available and include those whose the polar group is a non-dissociated hydrophilic group containing a multiplicity of oxygen functions (ether, alcohol) which engage in hydrogen bonding with water.

Those nonionic detergents which have been found to be especially advantageous result from the polymerization of several ethylene oxide units on an alcohol and are represented by the following structural formula:

\[ -\text{O}-(\text{CH}_2\text{CH}_2\text{O})_n\text{H} \]

wherein \( n \) is a positive whole number integer, preferably from 1 to 20 and \( R \) is either a hydrogen or an alkyl radical, preferably an alkyl radical of from 10 to 25 carbons. The most preferable nonionic detergents are the ethoxylated linear secondary alcohols, i.e., where \( R \) is a long chain linear hydrocarbon radical attached by an internal carbon atom. These nonionic detergents are especially advantageous as they are generally biodegradable.

When it is desirable to employ a solution for the hydrolytic enzymes, it is appropriate to utilize glycerine in an amount sufficient to act as a carrier for the hydrolytic system, preferably up to 5% glycerine by weight of the total system, although greater or lesser amounts of glycerine have proven quite useful.

Within the spirit of the invention it has been found that various other substances often desired in a complete detergent composition are compatible with the nonionic detergents and hydrolytic enzymes and can be incorporated in the detergent composition for their known and desirable properties and without detracting from the basic formula of the new detergent. For example, bacteriostats can be used to plate out from the detergent composition onto the cleaned surface, thus serving to prolong bacteriostatic and fungostatic action; optical brighteners can be employed to enhance the whiteness of the treated surface, while perfumes and insecticides contribute their obvious beneficial effects. The amounts of these ingredients incorporated in the detergent composition will depend, of course, on the extent to which the properties thereof are desired in the final product and within the practice of the art.

When a dry powdered composition is employed, the detergent, applied to a surface requiring cleaning, is combined with a small quantity of water. The resulting concentrated aqueous solution has the advantage of drying quickly after application and therefore, being easily and effectively removed from the treated material by, for example, vacuum cleaning. In such dry compositions, it is not necessary to incorporate a carrier such as glycerine as the enzymes remain substantially inactive when stored in the dry powdered formulation.

The nonionic enzyme-containing detergents disclosed herein are capable of being used to clean virtually any type of contaminated surface or material. This includes the cleaning of rugs, carpeting, upholstery, tile, the shampooing of domestic animals; commercial and household laundry cleaning of all types and all other cleaning operations where it is desired to remove dirt particles containing organic matter such as proteins, fats and starches which collect on the surface or in the fibers thereof.

The enzyme-containing detergent compositions of the present invention are adapted to cleaning operations at any temperature conventionally employed, but for preferred results temperatures around 100° F. should be employed. Such temperatures provide a two-fold advantage: (1) the enzyme activity is maximized, while (2) a minimum time is required to cool when rinsing.

Concerning other advantages previously mentioned, the enzymes continue to accelerate hydrolysis of related organic compositions for at least about 24 hours and, as a result, when discharged along with the waste water into a waste disposal system, the enzymes will catalyze the
hydrolysis of organic waste matter in, for example, the drain lines and sewage systems. This is especially advantageous since foam formed by the commercially available detergents is stabilized by proteins (usually present in amounts of up to 4%) and therefore gathers in waste disposal systems. This foam concentration inhibits the functioning of waste disposal systems and causes other rather well published problems such as pollution of streams, rivers and lakes. However, in a detergent according to the present invention the foam quickly breaks down and disappears by action of the enzymes incorporated therein. In addition, odor is substantially reduced or entirely eliminated.

To further illustrate the invention the following examples are provided. It should be understood that the details thereof are not to be regarded as limitations as they may be varied as will be understood by one skilled in this art.

**EXAMPLE I**

A solution was prepared by adding 20 cc. of water to 200 mg. of hydrolytic enzymes having 1.9×10⁶ units of activity per gram of enzyme, prepared as set forth in United States Patent No. 3,031,380, supra. The mixture was stirred until a clear brown solution was obtained and 30 cc. of 99% glycerine were added thereto and thoroughly mixed. Then 476 grams of a nonionic surface active agent (Sterox DJ) were added. The resulting mixture had a pH of about 7. Storage appeared to have no adverse effects on the level of enzyme activity.

To a washing machine filled with soiled linens and warm water there was added the composition set forth above. Similarly soiled linen was treated with the non-ionic detergent composition prepared without the enzyme. Both machines of linen were rinsed by conventional means.

The linens treated with the enzyme-containing detergent appeared cleaner, brighter and softer to the naked eye. Microscopic examination of the batches of linens revealed that cleaning of the linen subjected to the enzyme-containing detergent was thorough whereas that washed in the non-enzyme detergent still contained organic matter.

Additional tests with nonionic hydrolytic enzyme detergent compositions containing small amounts of various substances further substantiated the beneficial effect of the compositions of this invention. These tests included the addition of 0.5 gram of various optical brighteners, i.e., Tinopal 4BM, Tinopal RBS and the like; and 2.5 grams of various bacteriostats such as 3,4,4′-trichlorocarbanilide.

**EXAMPLE II**

A dry nonionic detergent composition was prepared by mixing 1000 grams of the nonionic surface active agent Pluronic F-68 with 2.6 grams of the hydrolytic enzyme of Example I. Again, lengthy storage appeared to have no adverse effect on the catalytic activity of the hydrolytic enzymes.

This composition was applied in an aqueous form to soiled wool carpeting and allowed to dry in place. The residue was removed by vacuuming. The enzyme-containing detergent hydrolyzed the organic matter clinging to the fibrous surface, loosening the soil so that it was more readily displaced therefrom than from a similar carpet treated with a non-enzyme-containing detergent.

In further tests substances possessing various beneficial attributes were included as part of the dry composition without adversely affecting the enzyme activity. These materials included 5.0 grams of 3,4,4′-trichlorocarbanilide, a bacteriostat; 2.5 grams each of Tinopal 4BM and Tinopal RBS 200, optical brighteners; and 15.0 grams of trisodium phosphate, a neutralizer for the optical brighteners.

Although the foregoing invention has been described in some detail by way of illustration and example for purposes of clarity of understanding, it will be understood that certain changes and modifications may be practiced within the scope of the invention as limited only by the scope of the appended claims.

What is claimed is:

1. A substantially non-aqueous enzyme-containing non-ionic liquid detergent suitable for removing organic-containing dirt particles from a contaminated surface, consisting essentially of: at least one protease enzyme in an amount up to about 1.0% by weight of the total composition; the remainder of said detergent having the structural formula:

\[ R-O-(CH₂CH₂O)ₙ-H \]

wherein \( n \) is a positive whole number integer of up to 20 and \( R \) is selected from hydrogen and an alkyl radical of from 10 to 25 carbons.

2. The liquid detergent system of claim 1 and further characterized by up to 5% water by weight of total composition.

3. A process for removing organic-containing matter from a contaminated surface comprising the steps of: preparing an aqueous solution of the liquid detergent system of claim 2, applying said aqueous solution to said surface; and thereafter removing said aqueous solution.

4. A liquid detergent in accordance with claim 1 and further characterized by up to about 5% glycerine by weight of total composition.

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