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AEROSOL ENZYME DETERGENTS STABILIZED WITH CARBON DIOXIDE

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ABSTRACT OF THE DISCLOSURE

Stable liquid or semi-liquid detergent compositions are provided, preferably in the form of foamy aerosols, containing hydrolytic enzymes stabilized by colloidal silica and/or dissolved carbon dioxide.

CROSS REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of application Ser. No. 56,638, filed July 20, 1970, now abandoned.

BACKGROUND OF THE INVENTION

Field of the invention

Hydrolytic enzymes have been recognized as useful adjuncts in detergent compositions. For the most part, the enzymes are included in dry granular media and regain their activity upon solution in water. While in the dehydrated state or dry state, the enzymes are stable for long periods of time under a wide variety of conditions of temperature, humidity and the like.

For certain applications, it is desirable to employ hydrolytic enzymes in the liquid state. With aerosols, the cleaning composition may or may not be introduced into an aqueous medium. Therefore, as part of the cleaning composition, the enzyme must be hydrated, in order to be active when applied to the surface to be cleaned.

Unlike dehydrated or dry enzymes, hydrated enzymes or enzymes in solution are much more sensitive to temperature, other chemicals, pH, and the like. Therefore, in commercial use, where the composition may be subjected to a wide range of temperature conditions, chemical interactions and the like, it is necessary that the enzyme be protected in order to retain its activity for use.

Furthermore, many of the enzyme compositions which find use in detergent compositions are proteolytic enzymes. That is, the enzymes are capable of hydrolyzing protein chains. Enzymes are protein chains. In the body, proteolytic enzymes are protected from degradation by another molecule of the same enzyme. However, in an in vitro environment, the protective mechanisms are not available, and the active enzyme may degrade another molecule of the same enzyme.

In developing detergent compositions containing enzymes, where the enzymes are hydrated prior to use, it is essential that the enzymes be protected from deactivation or denaturation by the surface active material. Furthermore, it is desirable that the enzyme be stable under normal conditions of packaging and shipping. In addition, it is essential that the mode used to protect the enzyme does not significantly affect the cleansing activity or capability of the enzyme.

Description of the prior art

Patents of interest include U.S. Pats. Nos. 3,033,691, 3,278,390, 3,506,582, 3,519,538, and 3,549,541.

SUMMARY OF THE INVENTION

Detergent compositions containing a minor amount of a hydrolytic enzyme and a substantial amount of a non-ionic detergent are combined with colloidal silica or dissolved carbon dioxide (carbonate) to provide detergent compositions which retain enzyme activity for long periods of time. These compositions find particular use as aerosols.

DESCRIPTION OF THE SPECIFIC EMBODIMENTS

The detergent enzyme compositions of this invention are useful in cleaning, surface preparation, processing, debridement, emollient creams, oils or lotions. Particular applications include shampoos, bathing preparations, skin creams and other body treatment compositions. In addition, if desired, the non-ionic detergent-enzyme composition can also be employed in solid form, such as bars.

The primary active ingredients in the subject compositions are a liquid non-ionic detergent and a hydrolytic enzyme, particularly a proteolytic enzyme. Included in the detergent composition is a small but sufficient amount of colloidal silica and/or dissolved carbon dioxide.

The compositions will normally have from about 10 to 60, more usually from about 15 to 50 weight percent of the non-ionic detergent based on the total composition. From about 1 to 15 weight percent of the non-ionic detergent may be substituted with an anionic detergent. The amount of enzyme will depend to a significant degree on the activity of the enzyme. With a wide variety of commercially available hydrolytic enzymes, useful amounts will be in the range of about 0.001 to 1 weight percent, more usually 0.005 to 0.5 weight percent based on the total composition. Water which is included in the composition will generally range from about 1 to 30 weight percent, more usually from about 3 to 20 weight percent.

The stabilizing ingredients are colloidal silica and carbon dioxide. The colloidal silica will generally be in amounts of from 0.01 weight percent to 10 weight percent, more usually from 1 to 5 weight percent. The amount of silica will generally be from 1 to 50 parts per part of enzyme. The carbon dioxide will generally be at least 0.01 weight percent, and usually be in the range of about 1 to 2 weight percent, conveniently at saturation of the system. Numerous other ingredients will also be included. Particularly in the aerosol with a haloorganic propellant, a halogen scavenger may be included in minor amounts. A useful halogen scavenger is sodium thiosulfate. To enhance the solubility of the carbon dioxide, various amines may be included, particularly triethanol amine. The amines will generally be present in minor amounts, the triethanol amine, when present, will generally be present in amounts of about 0.001 to 1 weight percent. The amounts indicated are based on the total composition.

In addition, heavy metal scavengers can be employed to advantage, particularly such scavengers as ethylene diamine tetraacetic acid.

To enhance the skin moisturizing qualities of the composition, various glycols may be used, such as propylene glycol, glycerine, and the like. These may be employed in large amounts varying from 1 to 60 weight percent, frequently from 5 to 50 weight percent of the total composition. Small amounts of oily materials may be used, such as lanolin or modified lanolins, e.g., ethoxylated lanolin. The amounts of lanolin or lanolin derivatives will generally range from about 0 to 10 weight percent, more usually from about 1 to 8 weight percent.

Other additives which may also be included are buffers, thickening agents, bacteriocides, and the like. In addition, minor amounts of materials to enhance market acceptability may also be incorporated, such as perfumes, optical brighteners, fillers and the like.

The compositions can be readily prepared by combining the various liquid or solid ingredients so as to obtain a substantially homogeneous composition. With carbon dioxide, the compositions can be pressurized with

carbon dioxide gas at super atmospheric pressures so as to insure saturation of the composition.

Normally, the order of preparing the composition is to hydrate the enzyme with water, and blend in the hydrated enzyme with the polyols, non-ionic detergent, optionally silica, and any other additives which are to be incorporated.

The individual ingredients of the subject composition will now be considered.

The first ingredient is the detergent, which is essentially a non-ionic liquid detergent, Anionic detergents, such as the alkylbezene sulfonate, and cationic detergents, can be mixed with the nonionic detergent in amounts of up to about 15 weght percent of the total detergent composition without severe loss of enzyme digestive action. In general the detergent portion of the inventive composition must consist of at least about 85 weight percent of non-ionic detergents with ionic detergents being limited in amounts to less than about 15% and preferably less than about 2 to 5%. Certain of the ionic detergents contribute to the foaming action of the detergent-enzyme composition but otherwise have no effect upon the inventive composition and generally do not change the fundamental characteristics of the enzyme-detergent compositions of the invention. In general, the detergents may be hydrophobic, hydrophilic, oleophobic or oleophilic in function.

Among these non-ionic detergents which are suitable for use in the compositions of this invention are the polyethylene oxide ether detergents referred to in Pat. Nos. 3,472,783 and 1,970,578 and the liquid non-ionic polyglycol type detergents referred to in the latter patent such as those obtainable by introducing the polyglycol radicals into the carboxylic acids to produce detergents of the general formula:

$$RCO—(—O—C_2H_4—)_x—O—CH_2—CH_2—OH$$

in which RCO is the acid radical of the carboxylic acid and x is 3 or an integral number greater than 3. Also included are those detergents obtainable by introducing the polyglycol radicals into amines to produce detergents corresponding to the general formula:

$$RNH—(OC_2H_4—)_x—O—CH_2—CH_2OH$$

in which RNH is the radical of an amine and x is 3 or an integral number greater than 3. Reference is made to the aforesaid Pat. No. 1,970,578, which is incorporated by reference, for a more complete discussion of these classes of detergents.

The liquid non-ionic detergents shown in Table I are suitable for use in the inventive compositions.

TABLE II

Trade name	Manufacturer	Chemical type
Acidolate	White Laboratory, Inc.	Sulfonated oil.
Alipal CO-433	GAF Corporation.	Sodium salt of sulfate ester of alkylphenoxypoly (ethyleneoxy) ethanol.
Alkanol BG	DuPont	Sodium alkylnaphthalene sulfonate.
Duponol 80	do	Sodium octyl sulfate.
Emcol 4100 M	Witco Chemical Corp.	Sodium sulfosuccinate.
Santomerse SX	Monsanto	Alkyl aryl sulfonate.

The cationic detergents listed in Table III are suitable for use in minor amounts in the inventive compositions.

TABLE III

Trade name	Manufacturer	Chemical type
Alacsan 7 LUF	Alcalac Chemical Corp.	Alkyl dimethylbenzene ammonium chloride.
Aromox DMM CDW	Armour Industrial Chemical Company.	Dimethylcocomine oxide.
Emcal CC-9	Witco Chemical Corp.	Polypropoxylated quaternary ammonium chloride.
Richmate 1655	The Richardson Co.	Amine salts.

In addition, amphoteric detergents such as Deriphat 151C, an N-coca-beta-amino propionic acid manufactured by General Mills Company, may be suitable for use in minor amounts in the inventive composititon s.

Other detergents and detergent compositions of the same or equivalent classes are also suitable for use in the inventive compositions.

The second ingredient is the enzyme.

The enzymes which are especially suitable for use in the inventive composition are the hydrolizing enzymes (hydrolyase) and, more specifically, the neutral protease, esterease, carbohydrase and nuclease enzymes.

The enzymes are commercially obtainable in dried, powdered form and may be stored in that form until incorporated in the subject compositions. The commercially powdered enzyme products generally are dried products comprising from about 2% to about 80% active enzymes in combination with an inert powdered vehicle. The actual active enzyme contents depends upon the method of manufacture and is not critical, so long as the detergent solution has the desired enzymatic activity.

Many commercial products contain proteases, preferred in this invention, as the active enzyme. In most cases, a subtilisin comprises the major part of the proteases. The

TABLE I

Trade name	Manufacturer	Chemical type
Alfonic Ethoxylate	Continental Oil Co	Ethylene oxide adduct of straight chain fatty alcohols.
Alkamine	Amalgamated Chem. Corp	Alkanolamine fatty condensate.
Allo-Scour DB	Scholler Bros., Inc	Ethoxylated alcohol.
Alrosol	Geigy Industrial Chemicals	Fatty alkylol amide condensate.
Antarox BL-330	GAF Corporation	Aliphatic polyether.
Emcal 5130	Witco Chemical Corp	Alkanolamine condensate.
Emcal DOS	do	Diethylene glycol oleate.
Energetic R	Armour-Dial, Inc	Polyethylene ester of fatty acid.
Energetic W-100	do	Fatty alcohol ethylene oxide condensate.
Hyonic LA-40	Nopco Chemical Div. of Diamond Shamrock Chemical Company	Fatty acid alkylolamide.
Igepal CA-620	GAF Corporation	Octylphenoxypoly (ethyleneoxy) ethanol.
Merpol HCS	DuPont	Ethylene oxide condensate.
Neodal 23-6.5	Shell Chemical Company	C_{12}–C_{13} linear primary alcohol ethoxylate.
Plurofac B-20	Wyondott Chemical Corp	Ethoxylated straight chain alcohol.
Polysorbate 80	Drew Chemical Company	Polyoxyethylene (20) sorbitan monooleate.
Teox 120	Olin Matheson	Polyethyleneoxy tallate.
Tergitol-12-M-10	Union Carbide	Dodecyl mercapto polyethylene glycol ether.
Triton B-1956	Rohm and Haas Co	Phthalic glycerol alkyd resin.
Triton CF-21	do	Alkylaryl polyether.
Triton DF-16	do	Polyethoxylated straight chain alcohol.
Triton N-57	do	Nonyl phenoxy polyethoxy ethanol.
Triton X-100	do	Octyl phenoxy polyethoxy ethanol.
Triton X-123	do	Alkyl benzyl polyethylene glycol ether.

The anionic detergents shown in Table II are suitable for use in the inventive compositions in minor proportions.

proteases useful in the invention may be either neutral or alkaline protease. Other enzymes which are useful in the

invention are the α-amylases, lipases, cellulases, tryptases and peptidases. In general, these enzymes are obtained through bacterial fermentation, although enzymes obtained from fungial fermentation or of animal origin may be included in the inventive compositions.

CRD protease, sold by Monsanto Chemical Company under the designation DA–10, is a useful powdered enzyme product which reportedly is obtained by mutation of a *Bacillus subtilis* organism. This enzyme is about 20% alkaline protease and about 80% neutral protease, the neutral protease having a molecular weight of about 44,000 and containing from 1 to 2 atoms of zinc per molecule. The particle size of this enzyme product is from about 0.03 mm. to about 0.01 mm.

Specific examples of commercial enzyme products include: Alcalase, Maxatase, Protease B–4000 and Protease AP, CRD-Protease, Viokase, Pronase-P, Pronase-AS and Pronase-AF, Rapidase P–2000, Takamine, Bromelain 1:10 HT proteolytic enzyme 200, Enzyme L–W (derived from fungi rather than bacterial), Rhozym P–11 concentrate, Pectinol, Lipase B, Rhozyme PF, Rhozyme J–25; Rhozyme PF and J–25 have salt and corn starch vehicles and are protease having diastase activity; Amprozyme 200.

The following patents and publications are incorporated herein by reference for a more complete discussion of enzyme technology and the methods of producing and preparing the enzyme suitable for use in this invention: Tauber, The Chemistry and Technology of Enzymes; White, Handler, Smyth, Steton, Principles of Biochemistry (1st ed., 1954), Dixon and Webb, Enzymes (2nd ed., 1964), Bergkvist, U.S. Pat. No. 3,281,331; Kita, U.S. Pat. No. 3,173,847; Smythe, U.S. Pat. No. 3,033,-691; Minagawa and Hamaishi, U.S. Pat. No. 3,031,380; Noe et al., U.S. Pat. No. 3,409,419; Roald et al., U.S. Pat. No. 3,451,935; Gore et al., U.S. Pat. No. 2,164,914.

The third ingredient is the colloidal silica.

The flamed colloidal silica component may typically contain approximately 14% by weight of aluminum oxide and remains inert to the enzyme and acts as an enzyme carrier and stabilizer. Bench tests indicate superior stability of the enzyme-detergent systems using silica in an amount of at least about 0.01% and up to about 10% by weight, and preferably from about 1% to about 4% or 5% by weight for liquid compositions with higher amounts useful in bar products. These tests were conducted under accelerated aging conditions using storage at 125° F. in a constant temperature oven for a period of one month. This simulates nine to ten months of shelf life at optimum temperature.

One silica of the type suitable for use in the present invention is manufactured and sold by Degussa, Inc., Pigments Division, 2 Pennsylvania Plaza, New York, N.Y. 10001, under the trademark Aerosil COK 84 and is composed of 86% silica and 14% aluminum oxide. The silica is inert and of a primary particle size of from about 20 to about 60 millimicrons and has a surface area of approximately 150, BET ($m.^2/g.$).

Another silica product identified by the trademark Aerosil 200 has also been used satisfactorily in the compositions of this invention. This product has a particle size of approximately 12 millimicrons and a surface area of 200.

Any conventional inert propellant may be used in combination with the compositions of this invention in packaging the enzyme-detergent composition in an aerosol container. Carbon dioxide, which is highly soluble in the liquid detergent-enzyme composition, does not constitute a propellant per se but such inert gases as nitrogen are suitable propellants. The light hydrocarbons, propane, butane, etc., are also suitable propellants. Carbon oxide (monoxide), which is inert to most enzymes of interest, could be used but is not desirable in a consumer product.

The inert fluorinated hydrocarbons, Freon-11 and Freon-12, for example, may also be suitable as propellants for the aerosol composition of the invention, although the enzymes may perhaps be less stable in the presence of such propellants than in the presence of an inert gas such as nitrogen.

The enzyme-detergent compositions of this invention when formulated and used for industrial or household laundry purposes, result in instant enzyme activity. As soon as the aerosol enzyme-detergent composition is introduced into the washing machine with warm water, the carbon dioxide flashes off and the enzyme activity reaches a maximum substantially instantaneously. This results in maximum enzyme cleaning effect and maximum utilization of available enzymes. Less expensive and more effective enzyme detergents are, therefore, possible using the techniques and principles of this invention. Moreover, the enzyme activity is stabilized and remains effective for a longer period of time. Even where the enzyme-detergent compositions of the invention are used in conjunction with ionic detergents, the enzyme activity remains high because of the stabilizing effect of the colloidal silica.

The colloidal silica stabilized enzyme detergent systems have a long shelf life and even enhanced stabilization when the enzyme-detergent system is diluted with large quantities of water. For example, enzyme activity of a dilute water solution of non-ionic liquid detergent-enzyme composition diminishes rapidly over several hours and most of the activity has disappeared at the end of 24 hours, more or less depending on the environment. In contrast, enzyme activity of enzymes of the same type in a dilute water solution of the non-ionic liquid detergent-enzyme-silica compositions of this invention was very high after 46 days in water at 82–86° F. These tests indicate an enzyme activity after 46 days in dilute water solution which is approximately the same as the initial enzyme activity.

The silica gives the composition a thixotropic characteristic; the thickened liquid acts as an enzyme carrier and remains in intimate contact with the skin utilizing the natural moisture of the skin to catalyze digestion of the horny layer or keratin plug, sebaceous oils and like secretions. The non-ionic detergents cleanse the skin of inert soils and the foam phenomena of high-foaming non-ionic or ionic detergents aid in the mechanical removal of the soils, as well as providing the aesthetic lather effect which is commonly identified with cleansing action.

The following examples illustrate the invention:

EXAMPLE I

An aerosol package was prepared with the following formulation:

	Parts
Enzyme—Monsanto Subtilo peptidase A type; 1.9×10^6 u./g. activity [1]	[2] 0.01
Water	15
Glycerine (99%)	30
Propylene glycol	21
Non-ionic detergent—Triton X–100 (octyl phenoxy polyethoxy ethanol)	26
Ionic detergent—F–90 (linear alkylbenzene sulfonate salt)	4.5
Lanolin—Lanatox 55 (ethoxylated lanolin)	5
Triethanolamine	2
Perfume	Trace
Carbon dioxide	1–2
Propellant—1:1 mixture of Freon 11 and Freon 12	(3)

[1] Prepared by the process described in U.S. Pat. No. 3,301,380 to Minagowa et al. The enzyme concentrate is about 2×10^6 u./g. in amylase activity.

[2] This amount of enzyme in the formulation results in a specific activity of about 1.3 units per gram in the diluted enzyme-detergent system when diluted at a ratio of 1000 to 1, and an inhibited specific activity of 1.3×10^3 units per gram in the undiluted composition.

[3] Since the propellant is inert chemically, the proportions are not important chemically and were not determined. Propellant is added using standard techniques and amounts are determined using usual criteria to obtain a commercially desirable product appearance.

The resulting product was stable for several months at ambient temperature. When diluted in the ratio of 10 g. of detergent to 8 oz. of tap water, the resulting solution commenced significant attack on photographic film emulsion within 15 minutes and had stripped the emulsion from the substrate in less than one hour and retained its activity for at least about 3 months.

By way of comparison, the same composition when diluted in the same ratio with carbon dioxide saturated water (Canada Dry "Sparkling" water) did not begin attack on the film for almost an hour but the rate of attack was more rapid than in the former case once it began.

Stripping tests were run in stoppered graduate cylinders containing the solution into which a strip of Kodak Kodacolor film was partially immersed. Stripping was visually observed.

In another embodiment of the invention, the same principles and similar techniques and related methods are utilized to prepare a liquid composition which may be modified to provide a powdered or granulated detergent composition. One embodiment is illustrated in the following example.

EXAMPLE II

A first detergent-enzyme composition, designated here as mixture A, was prepared from the following components:

Monsanto AP neutral proteolytic enzyme, 2.56×10^6 u./g. activity protease, $.65\times10^6$ u./g. activity α-amylase ----------grams--	20
Monsanto Alk alkaline proteolytic enzyme, $.65\times10^6$ u./g. activity alkaline protease, nil activity neutral protease, trace activity carbohydrase --do----	20
Water (deionized) ----------mls--	100
Glycerine ----------grams--	200
Triton X–100 non-ionic detergent --------do----	2000

The enzymes, in powder form, were first dissolved in the water. Glycerine was added followed by addition of the liquid detergent, Triton X–100.

A second composition, mixture B, was prepared by dispersing 60 grams of Aerosil COK–84 silica in 225 grams of mixture A and mixing this dispersion into the remainder of mixture A, the combination being referred to here as mixture B.

A third composition, a detergent-enzyme additive concentrate, referred to here as mixture C, was prepared by thoroughly mixing 225 grams of liquid decanted from mixture B with 100 grams of COK–84 silica. The resulting product was a fine, free flowing powder having a particle size of about 20 mesh. This product, mixture C, is suitable for handling, shipping and sale for addition to various detergents, builders, whiteners, etc. to produce a commercial household and industrial detergent. One embodiment of such a detergent was prepared by mixing 285 grams of mixture C with the following ingredients:

	Grams
G.A.F. Igepal DM–970 non-ionic detergent, 100% active detergent in brittle flake form ----------	144
G.A.F. Igepon T–77 non-ionic detergent, 67% active detergent in flake form ----------	140
G.A.F. Igepon T–734 non-ionic detergent -------	75
Sodium sulfate ----------	1300
Carboxymethyl cellulose ----------	30
Sodium borate ----------	510
Polyvinylpyrrolidone ----------	1
G.A.F. Lancophor RG optical brightener ---------	6
3,4,4'-trichlorocarbanilide bacteriostat ----------	12
Aerosil COK–380 silica (for flow control) ------	85
Potassium carbonate ----------	300
Potassium silicate ----------	150
Perfume ----------	5

The resulting product was a homogeneous, free flowing granular powder product which had excellent cleaning properties and exhibited no tendency to segregate in laboratory handling. The detergent, containing the enzyme activity, digested the emulsion from Kodak Kodacolor movie film in less than 15 minutes at 120° F. the normal wash cycle. By comparison, Procter and Gamble's commercial detergent Tide XK had not digested the emulsion in 48 hours under similar conditions.

When used in a home laundry, the aerosol enzyme-detergent system did not give the "pinhole" effect often observed when powdered enzyme detergents or enzyme presoak products are used. The "pinhole" effect results, apparently, from contact of solid undissolved enzyme-containing particles on the fabric and subsequent dilution, which results in an extremely high enzyme activity at the point of contact. Enzyme activity is achieved immediately upon contact with the warm water and is quickly distributed throughout the wash water.

Obvious variations, using the normal skill of the detergent formulator, can be made based on the foregoing. For example, many types and classes of detergents, fillers, brighteners, flow control agents, etc., may be selected according to the characteristics desired in the end product, the particular advantages and disadvantages of given materials for specific end uses, etc.

Indeed, many variations of the invention generally and of the specific facets, embodiments, examples, etc., may be made by one skilled in the art without departing from the spirit and scope of the invention.

What is claimed is:

1. A detergent composition having 15 to 50 weight percent of a non-ionic detergent with up to 15 weight percent of said non-ionic detergent substituted by an anionic detergent, from 0.05 to 0.5 weight percent of a proteolytic enzyme, at least one of from 0.01 to 10 weight percent of colloidal silica or from 0.01 to 2 weight percent of dissolved carbon dioxide, and from 1 to 30 weight percent of water.

2. A detergent composition according to claim **1**, having from 0.001 to 1 weight percent of triethanol amine.

3. A detergent composition according to claim **1**, having from 1 to 60 weight percent of a moisturizing glycol.

4. A detergent composition according to claim **1**, having from 0 to 10 weight percent of lanolin or a lanolin derivative.

5. An aerosol composition comprising a detergent composition according to claim **1** and an inert propellant.

6. An aerosol composition according to claim **5**, wherein said propellant is a haloorganic gas.

References Cited

UNITED STATES PATENTS

3,549,541	12/1970	Reinish ----------	252—89
3,519,538	7/1970	Messing et al. --------	195—63
3,506,582	4/1970	Gertzman ----------	252—89
3,278,390	10/1966	Arthur ----------	195—63
3,033,691	5/1962	Smythe et al. --------	252—89
1,679,250	7/1928	Lind ----------	252—89

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