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(54) **Enzymatic drain cleaning compositions.**

(57) The present invention provides a composition for cleaning drains clogged with a hair-containing deposit which comprises: (a) a hair-disintegrating amount of a proteolytic enzyme, (b) a disulfide reducing agent, and (c) an alkali metal bisulfite compound in an amount sufficient to enhance the rate of activity of the enzyme, wherein the components (a), (b) and (c) are present as dispersions, separately or in combination, in water-soluble beads, each comprising a water-soluble polymer, such that the enzyme and reducing agent cannot substantially cross-react prior to dissolution of the beads, and wherein the composition on dissolution provides a pH that enhances hair denaturation.

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ENZYMATIC DRAIN CLEANING COMPOSITIONS

Technical Field

The present invention relates to enzymatic drain cleaner compositions. Specifically, the invention relates to such compositions wherein the components are mixed with a water soluble polymer and formed into beads and which have enhanced enzymatic activity.

Background of the Invention

Bathroom sinks, tubs and shower drains can become clogged when deposits containing hair accumulate in such areas as the drain sink trap, thereby preventing or impeding water from draining properly. A wide variety of preparations are available for dissolving and removing such deposits. Most conventional drain cleaning products contain caustics, such as strong sodium hydroxide. The alkali saponifies whatever fatty material is present in the deposit such that it is converted into a water soluble soap or a softened, water-dispersible material. If the clog is due to hair, the caustic acts as a degradative agent, but is only partially effective, as tested in laboratory simulations. Further, caustic materials are poisonous and can damage many conduit materials and injure people on contact.

Another disadvantage of these drain cleaners is that they are not site specific. That is, if the drain cleaner has to pass through a column of backed-up water to reach the clog, as is often the case, a portion of the active ingredient can dissolve in the water away from the clog. This portion is wasted, and the concentration of active ingredient at the clog site is correspondingly diminished.

A second method for unclogging drain lines involves mechanically cutting through the deposit. This method, however, is practical only if the deposit clogging the drain can be reached by mechanical means without having to dismantle part of the drain line.

The hazards and disadvantages of these conventional methods have led to searches for alternate and better methods of cleaning drain lines clogged with deposits containing hair. One alternative route has involved the use of enzyme-containing compositions. Enzymes can convert common drain clogging materials to water soluble materials which can be removed easily. A drawback to their use has been their short shelf life which, in many cases, is attributable to interaction between the various components of the enzyme system. This interaction is aggravated at high temperatures, such as those which can be encountered during shipment of the enzyme preparation. Further, for enzymes to be most effective in the solubilization of animal proteins such as hair, their use must be preceded by a breaking down of the protein material to expose it to enzymatic action.

Recently, drain cleaner compositions have been made which are site specific and provide a sequential activity of ingredients for enzymatic dissolution of protein. These compositons comprise a plurality of water soluble beads, wherein each bead comprises a mixture of at least one active drain cleaning ingredient dispersed in a water soluble polymer such that cross-reactive ingredients cannot react with one another prior to dissolution of the polymer. These compositions have proven effective in unclogging drains clogged with hair or a hair-containing deposit. Improvements are desired, however, to further enhance the activity of the proteolytic enzyme in the drain.

Accordingly, it is an object of the present invention to develop an enzymatic drain cleaner bead composition with increased enzymatic activity. Additional objectives of this invention will become apparent from the following disclosure.

According to one aspect of the present invention, there is provided a composition for cleaning drains clogged with a hair-containing deposit which comprises: (a) a hair-disintegrating amount of a proteolytic enzyme, (b) a disulfide reducing agent, and (c) an alkali metal bisulfite compound in an amount sufficient to enhance the rate of activity of the enzyme, wherein the components (a), (b) and (c) are present as dispersions, separately or in combination, in water-soluble beads, each comprising a water-soluble polymer, such that the enzyme and reducing agent cannot substantially cross-react prior to dissolution of the beads, and wherein the composition on dissolution provides a pH that enhances hair denaturation.

Description of the Drawing

Figure 1 presents two distribution plots showing the percentage of hair degraded in trials with two different formulations, one which contains sodium bisulfite and one which does not.

Detailed Description of the Invention

The present invention relates to enzymatic drain cleaner compositions which are capable of degrading hair-containing deposits in drain pipes and have enhanced enzymatic activity.

Commonly assigned U.S. Patent Application Serial Number 622,141, filed October 17, 1984, discloses

enzymatic drain cleaning compositions which comprise a plurality of water soluble beads which comprise one or more proteolytic enzymes, a disulfide reducing agent, or a combination thereof, dispersed in a water soluble polymer such that cross-reactions between the enzyme(s), the reducing agent, and any other optional ingredients which may be added cannot occur prior to the dissolution of the polymer. In these compositions, the disulfide reducing agent acts to break the disulfide bonds through which cysteine cross-links hair proteins into a crstalline structure. The cross-linked crystalline form is highly resistant to proteolytic enzymes alone, but once the disulfide bonds are broken the proteolytic enzyme can act to break the covalent backbone of the protein (i.e., to hydrolyze the peptide bonds of the protein).

Applicants now have discovered that the rate of effectiveness of these compositions can be enhanced by adding an alkali metal bisulfite compound to the composition. A preferred compound is sodium bisulfite. It is theorized that, within certain concentrations, these bisulfite compounds modify the proteolytic enzymes of the composition such that their rate of activity is enhanced. Generally, the amount of bisulfite added to enhance the activity of the enzyme is within the range of about 0.001 to about 0.1 weight percent of the total composition. If the bisulfite compound is added at a concentration outside this range, it typically either has no noticeable effect on enzyme activity or appears to inhibit activity. When the activity enhancer is sodium bisulfite, it preferably is added such that it comprises about 0.04% by weight of the final composition.

In one embodiment of the invention, the bisulfite compound is included in the composition by mixing it with the alkaline protease before the latter is dispersed in

the water soluble polymer and formed into beads. The weight to weight ratio of protease to alkali metal bisulfite generally ranges from about 10:1 to about 1000:1 and preferably ranges from about 50:1 to about 500:1.

When the bisulfite compound is mixed with the alkaline protease it can serve not only to enhance the activity of the protease but also as an anti-microbial agent. It has been found that when the source of the proteolytic enzyme in the composition is a fermentation broth, the enzyme containing beads can, over time, show signs of microbial growth. The addition of an alkali metal bisulfite compound, however, such as sodium bisulfite, can prevent or retard microbial growth on the beads during storage.

Proteolytic enzymes useful in dissolving hair are those which are active under neutral to alkaline conditions. Preferred enzymes are derived from microorganisms of the genus Bacillus, such as B. subtilis or B. amyloliquefaciens. In addition, enzymes such as the plant protease papain or the alkaline protease from Streptomyces griseus may be used. A single protease or a mixture of several different proteases can be used. Disulfide reducing agents include any which function at an alkaline pH to soften hair structure. Preferred disulfide reducing agents include thioglycolates, as, for example, the calcium, ammonium, potassium and sodium salts of thioglycolic acid. Other disulfide reducing reagents, such as -mercaptoethanol, may be used. Preferred are sodium and potassium thioglycolate.

These various enzyme-containing compositions optionally may contain other ingredients which act to enhance the enzyme's drain cleaning ability. For example, as noted previously, the enzymes cited above typically are active within a particular pH range. One

component of the drain cleaning beads of this invention may be a buffer to maintain a pH that enhances hair denaturation. Other optional additives include detergents, stabilizers and thickening agents. The detergents may be anionic or nonionic compounds, including sodium dodecyl sulfate, octyl phenoxypoly-ethoxyethanol and polyoxyethylene sorbitan mono-oleate. A preferred detergent is sodium dodecyl sulfate. Suitable thickening agents include hydroxy-ethyl cellulose, polyacrylamide and derivatives of xanthan gum. A preferred stabilizer is N,N,N',N'-tetrakis (2-hydroxy-propyl)ethylene diamine. These various optional ingredients can be added in amounts sufficient to enhance enzymatic activity.

The protease, bisulfite compound and disulfide reducing agent may be contained in separate beads or may be combined into the same beads. In the latter case, the active components can be layered in the beads, such that the sequence at which the components reach the clog can be ordered. For instance, the protease and bisulfite compound can be mixed together and then formed into an inner layer with the polymer, then coated with an outer layer comprising the reducing agent. When the beads are added to water standing in the drain, the outer layer of the beads will dissolve most quickly, releasing the disulfide reducing agent to the clog. As the reducing agent acts on the cysteine bonds of the hair, the remainder of the beads dissolve, releasing the enzyme which can then attack the hair. Alternatively, the disulfide reducing agent, protease, bisulfite and any optional ingredients, such as a buffer, can be uniformly dispersed throughout the polymer in the same beads.

An example of a suitable water-soluble polymer is polyethylene glycol (PEG) having a molecular weight of from about 6,000 to about 20,000. Higher molecular

weight PEG is produced by linking 2 or 3 smaller polymer chains with epoxy linkers. Generally, the amount of polymer in each bead is from about 40 to about 99% by volume, with about 60 to about 80% preferred. The remaining portion comprises the active ingredient(s) and water. The actual concentration of polymer in the various beads will depend on the nature of the component, that is, whether the ingredient is an enzyme, detergent, reducing agent, etc., and on the need or desirability for making a final product wherein the different components will react in the drain in an ordered or sequential manner. The weight to weight ratio of the various active ingredients in the compositions of this invention to the polymer and the ratio of the active ingredients to one another can vary, depending upon a variety of factors, including the strength of the enzyme(s) and the presence of various optional ingredients. For example, in a bead composition wherein certain beads comprise the enzyme(s) and alkali metal bisulfite compound and other beads comprise the disulfide reducing agent, about 5 to about 50% of the beads can comprise a mixture of alkaline protease and bisulfite compound dispersed in polyethylene glycol, the weight to weight ratio of enzyme and bisulfite compound to PEG ranging from about 1:1 to about 1:1000, and about 50 to about 95% of the beads comprise a mixture of a disulfide reducing agent dispersed in PEG, the weight to weight ratio of reducing agent to PEG ranging from about 1:1000. Optionally, about 0.1 to about 20% of the beads can comprise a mixture of an additional ingredient, such as sodium dodecylsulfate, dispersed in PEG, the weight to weight ratio of SDS to PEG ranging from about 1:1 to about 1:1000.

Both dissolution time and melt temperature are affected by the amount of moisture in the polymer coating. Generally, the moisture content is less than

about 10% of the polymer by volume and preferably ranges from about 0.01 to about 2%. Bead diameter can vary from less than 1/2 millimeter to greater than 7 millimeters. Preferably, bead diameter is between about 0.5 millimeters and about 5 millimeters.

The enzymes and other components may be in either liquid or solid form. The enzyme source, for instance, may be either a fermentation broth or a dried enzyme powder. In either case, the polymer is melted, then mixed with the liquid or solid component of the drain cleaning composition. The beads, or pellets, then can be formed in a variety of ways. For example, the polymer-component mixture can be formed into droplets, then resolidified. Alternatively, the liquid mixture can be spread into a thin sheet which is ground into particles after it has resolidified. In addition, the material can be extruded and cut. The word "bead" as used throughout this application is intended to apply to all of these embodiments.

The following examples are provided to illustrate the present invention but are not to be construed as limiting.

Example 1

Two drain cleaner bead products were prepared. One had three different types of polymer-encapsulated active ingredients: sodium dodecylsulfate (SDS), a high alkaline protease (obtained from Enzyme Development Corporation), and sodium thioglycolate (Na-TGA). The other had two different active ingredients: NaTGA and a mixture of enzyme and sodium bisulfite (SBS). The SBS was added in an amount such that the liquid prepolymer contained 0.05% SBS. The polymer used was polyethylene glycol (Fisher Brand PEG_{8000}). The beads were produced by extruding a mixture of the active ingredient and the polymer through

a needle. Table II below lists the active ingredients and the conditions under which the beads were produced.

TABLE I

Bead Production Parameters

Product Bead Type	Needle Gauge	Average Product Bead Diameter	Column Water Jacket Temperature	Ratio of PEG*:active Component: H_2O	Active Component Concentration
SDS	18g	3mm	75°C	12:3:2	19%
Na-TGA	18g	4mm	80°C	3:1:0.23	25%
High Alkaline Protease	18g	4mm	55°C	17:8:0**	32%
High Alkaline Protease + SBS	18g	4mm	55°C	17:8.0	32%

* PEG_{8000} lab source - Fisher; Commercial Source - BASF Wyandotte

** The protease is purchased as an aqueous solution. The zero in the ratio indicates that no additional water is added.

The appropriate amount of polymer was weighed out into a beaker and heated at low heat (55°C-65°C) on a hot plate (non-stirring). A Pharmacia K16 column was connected to a heating water bath and the temperature adjusted accordingly (see Table I). The active component was then added to the PEG and mixed well. In the case of enzyme beads, the enzyme solution was added just prior to bead production, the mixture being stirred only one to two minutes before being poured into the column to prevent deactivation of the enzyme. Additional water was added as indicated on the chart. The same general procedure was used to make the enzyme-SBS beads, with the exception that the SBS was added to the enzyme solution

prior to mixing it with the PEG. In the case of SDS beads, the mixture was stirred gently to avoid foaming of the detergent, which creates bubble problems in the column. Sodium thioglycolate (Na-TGA) was made by adding sodium hydroxide to thioglycolic acid. Excess base was added so that the pH of the final formulation at the drain site could be adjusted to enhance the activity of the enzyme. In the initial step, NaOH pellets were ground and slowly added to liquid thioglycolic acid (on ice) and mixed until all had been added. This mixture was ground again and stored in a plastic container to preserve the stability of the compound until used in bead production. To produce the beads, the NA-TGA was mixed with the proper amount of water (see Table I). The resulting mixture was then ground and added to the PEG. The pre-polymer solution of each component was individually poured into the column and the column top piece secured. Air then was pumped via a Masterflex pump (using pump head size 7014 and compatible tubing) through the central inlet valve of the top piece, producing internal air pressure. The pre-polymer solution was thus forced through the column bottom piece and connected stainless steel valve, and then through and out of a needle of appropriate gauge, as indicated in Table II. The column bottom piece tubing connector, valve and needle were wrapped with heat tape and regulated to the same temperature as the column. The air flow rate was adjusted accordingly to insure individual bead formation. Droplets from the needle were allowed to fall onto a rotating disc to form beads. Cool air was blown over the beads to aid in rapid solidification. Alternatively, a refrigerated surface can be used. Beads then pass a stationary scraper which removes the beads from the rotating disc and deposits them into a collection vessel.

Example II

Activity of Alkaline Protease with Sodium Bisulfite (SBS)

The effect of sodium bisulfite on protease activity was measured by adding various amounts of SBS to aliquots of a fermentation broth containing a high alkaline protease (obtained from Enzyme Development Corporation). The samples then were assayed via the standard casein substrate assay procedure. The results of the test are set forth in the table below:

% SBS Added	Relative Activity
0	100
0.005	109
0.05	117
0.2	108
0.5	98

In a follow-up test, relative activity was measured by comparing several samples of protease-containing fermentation broth with samples of the broth to which 0.05% SBS had been added. For each run, two samples of fermentation broth were obtained from the same source at the same time, then SBS was added to one sample. The samples were assayed as before. The results are shown in the following table:

Run	Assay Value	
	Protease	Protease With 0.05% SBS
1	384	459
2	375	453
3	337	415
4	363	487
Avg.	365	454

The average increase in activity for those samples containing the 0.05% SBS was 24%.

Example III

Two sets of bead formulations were produced by the general procedure of Example I. One set comprised 3 types of beads, one comprising the protease, one comprising sodium dodecylsulfate and one comprising sodium thioglycolate (NaTGA). The other set was a 2 bead formulation, one type of bead comprising the protease and 0.05% SBS and the other comprising sodium thioglycolate. To each of 10 test tubes 2 grams of dry hair were packed and 50 ml. of water were added. To half of these test tubes were added 5 g. of the first beaded product described above; to the other half were added 5 g. of the second beaded product (containing the SBS). The first beaded product consisted of 1.56 gms enzyme beads, 0.78 gms of SDS beads and 3.52 gms. of NaTGA beads. The second beaded product consisted of 1.56 gms of enzyme plus SBS beads and 3.52 gms of NaTGA beads. The beads were added to the respective test tubes and allowed to stand unstirred for 16 hours. The hair from each test tube was removed, washed, dried and weighed to determine the total amount of degradation. The results are shown below:

	Grams Enzyme	Grams ~~SDS~~	Grams NaTGA	Grams Enzyme-SDS
Formulation I	1.56	.78	3.52	--
Formulation II	-	-	3.52	1.56

Tube No.	Formulation Added	Grams Hair Remaining (Dry Weight)	Percent Hair Degraded	Average % Degraded Per Formulation
1	I	.1656	91.7	
2	I	.2754	86.2	
3	I	.2985	85.1	86.0
4	I	.3941	80.3	
5	I	.3463	82.7	
6	II	.0702	96.5	
7	II	.1487	92.6	
8	II	.0832	95.8	91.4
9	II	.2745	86.3	
10	II	.2679	86.6	

Example IV

The procedure of Example III was repeated with the exception that each formulation was tested in twenty six test tubes rather than five. The results of the test are shown in Figure 1 which represents a distribution plot of the percentage of hair degradation for each formulation. The x-axis of each plot represents the percent of degradation, and the y-axis represents the frequency, or number of test tubes in which the different percentages of degradation (rounded to the nearest whole number) actually occurred. As the two graphs show, the average percentage of hair degradation was higher for the bead formulation containing SBS.

CLAIMS:

1. A composition for cleaning drains clogged with a hair-containing deposit which comprises:

(a) a hair-disintegrating amount of a proteolytic enzyme,

(b) a disulfide reducing agent, and

(c) an alkali metal bisulfite compound

in an amount sufficient to enhance the rate of activity of the enzyme,

wherein the components (a), (b) and (c) are present as dispersions, separately or in combination, in water-soluble beads, each comprising a water-soluble polymer, such that the enzyme and reducing agent cannot substantially cross-react prior to dissolution of the beads, and wherein the composition on dissolution provides a pH that enhances hair denaturation.

2. A composition as claimed in claim 1 which comprises:

(a) beads comprising a mixture of the proteolytic enzyme and bisulfite compound dispersed in a water soluble polymer and

(b) beads comprising the disulfide reducing agent dispersed in a water soluble polymer.

3. The composition of claim 1 wherein the proteolytic enzyme, disulfide reducing agent, and alkali metal bisulfite are each dispersed uniformly throughout the beads.

4. A composition as claimed in claim 1 wherein each bead comprises at least two layers, one layer comprising the proteolytic enzyme mixed with the alkali metal bisulfite and dispersed in the water soluble polymer and one layer comprising the disulfide reducing agent dispersed in the water soluble polymer.

5. A composition as claimed in any one of claims 1, 2, 3 and 4 wherein the alkali metal bisulfite is sodium bisulfite.

6. A composition as claimed in any one of claims 1 to 5 wherein the weight ratio of proteolytic enzyme to bisulfite compound ranges from about 10:1 to about 1000:1.

7. A composition as claimed in any one of claims 1 to 6 wherein the bisulfite compound is present in an amount of about 0.001 to about 0.1 weight percent of the total composition.

8. A composition as claimed in any one of claims 1 to 7 wherein the composition also comprises a buffer, detergent, thickening agent or stabilizer.

9. A composition as claimed in claim 8 wherein N,N,N', N'- tetrakis (2-hydroxypropyl) ethylene diamine is present as a stabilizer.

10. A composition as claimed in any one of claims 1 to 9 wherein the water soluble polyer is polyethylene glycol.

11. A composition as claimed in any one of claims 1 to 10 wherein the beads comprise about 40% to about 99% by volume water-soluble polymer.

12. A composition as claimed in any one of claims 1 to 11 wherein the beads have a diameter of about 0.5 to about 7 millimetres.

13. A composition as claimed in any one of claims 1 to 12 wherein the proteolytic enzyme is a bacterial or plant protease or mixture of proteases.

14. A composition as claimed in any one of claims 1 to 13 wherein the disulfide reducing agent is a thioglycolate.

15. A composition as claimed in any one of claims 1 to 13 wherein the disulfide reducing agent is β-mercaptoethanol.

16. A composition as claimed in any one of the preceding claims wherein the weight to weight ratio

of proteolytic enzyme to disulfide reducing agent is from about 1:1 to about 1:200.

17. A composition for cleaning drains clogged with a hair-containing deposit which comprises:

a plurality of water soluble beads wherein about 5% to about 50% of the beads comprise a mixture of an alkaline protease and sodium bisulfite dispersed in polyethylene glycol (PEG), the weight to weight ratio of protease to sodium bisulfite ranging from about 10:1 to about 1000:1 and the weight to weight ratio of protease and sodium bisulfite to PEG ranging from about 1:1 to about 1:1000; and

about 50% to about 95% of the beads comprise a mixture of sodium thioglycolate dispersed in PEG, the weight to weight ratio of sodium thioglycolate to PEG ranging from about 1:1 to about 1:1000.

18. A method for cleaning a pipe clogged with a hair-containing deposit which comprises contacting the deposit with a composition which comprises:

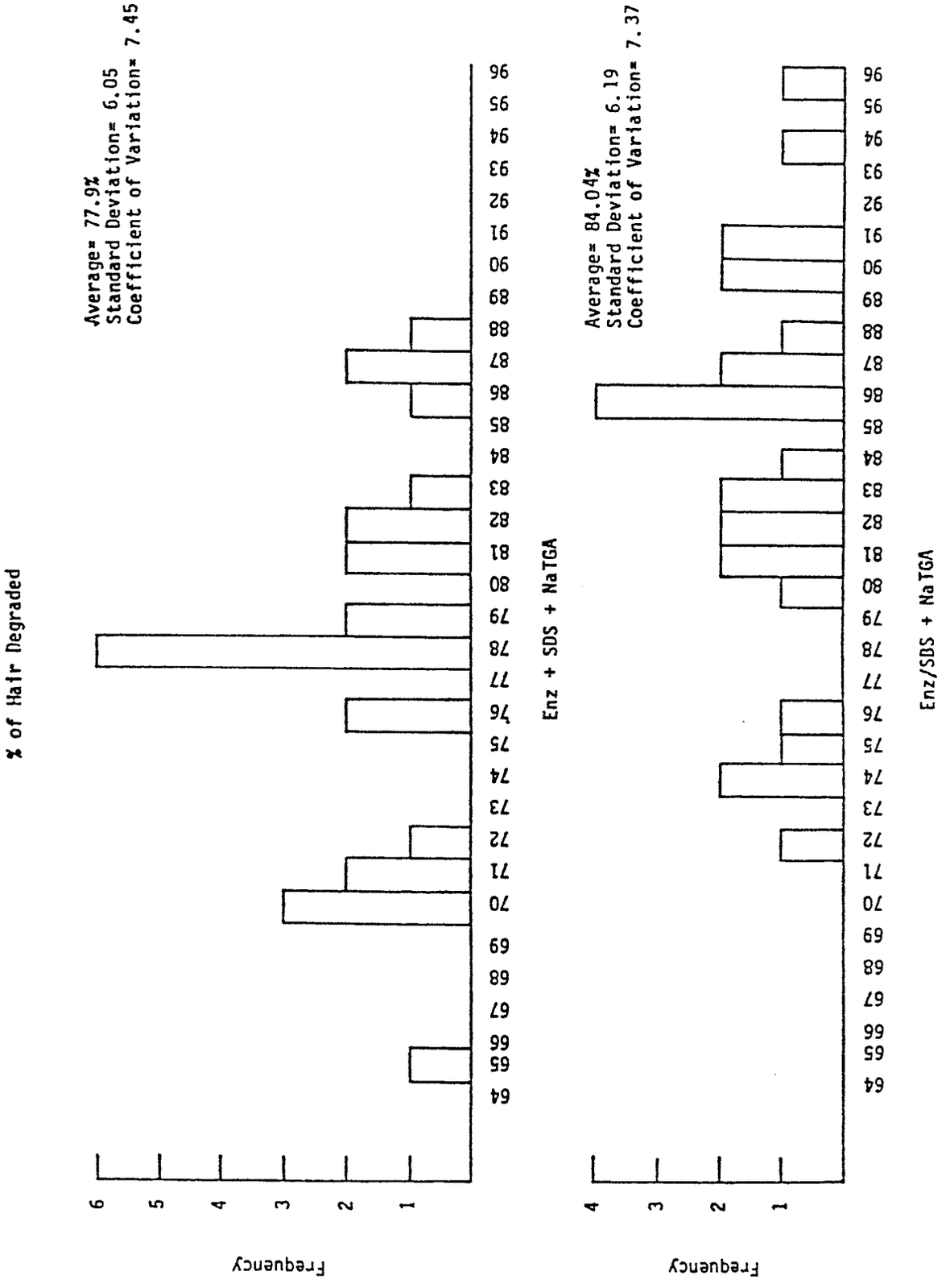
(a) a hair-disintegrating amount of a proteolytic enzyme,

(b) a disulfide reducing agent, and

(c) an alkali metal bisulfite compound in an amount sufficient to enhance the rate of activity of the enzyme,

wherein the components (a), (b) and (c) are present as dispersions, separately or in combination, in water-soluble beads, each comprising a water-soluble polymer, such that the enzyme and reducing agent cannot substantially cross-react prior to dissolution of the beads, and wherein the composition on dissolution provides a pH that enhances hair denaturation.

Figure 1


Average= 77.9%
Standard Deviation= 6.05
Coefficient of Variation= 7.45
% of Hair Degraded
Enz + SDS + NaTGA
Frequency
Average= 84.04%
Standard Deviation= 6.19
Coefficient of Variation= 7.37
Enz/SDS + NaTGA
Frequency