

⑫ **EUROPEAN PATENT APPLICATION**

⑲ Application number: 85307500.0

⑤① Int. Cl.⁴: **C 11 D 3/386**
C 11 D 17/00

⑳ Date of filing: 17.10.85

③① Priority: 17.10.84 US 661957
15.07.85 US 754576

④③ Date of publication of application:
23.04.86 Bulletin 86/17

⑥④ Designated Contracting States:
AT BE CH DE FR GB IT LI LU NL SE

⑦① Applicant: GENEX CORPORATION
6110 Executive Boulevard
Rockville Maryland 20852(US)

⑦② Inventor: Swann, Wayne Elliot
5392 Storm Drift
Columbia Maryland 21045(US)

⑦③ Inventor: Raymond, Lisa Grayson
P.O. Box 616 20 Bolleau Court
Middletown Maryland 21769(US)

⑦④ Representative: Holmes, Michael John et al,
Frank B. Dehn & Co. European Patent Attorneys Imperial
House 15-19 Kingsway
London, WC2B 6UZ,(GB)

⑤④ Composition for cleaning drains.

⑤⑦ The present invention provides a formulation for cleaning drains clogged with organic material deposits which comprises 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 the active ingredient is substantially chemically isolated from any other active ingredient present in the same bead and the active ingredient or ingredients in the other beads prior to dissolution of the polymer. In one embodiment, the product additionally comprises a liquid component which comprises one or more active drain cleaning ingredients, wherein the active ingredient(s) in the beads and the active ingredient(s) in the liquid are kept substantially chemically isolated from one another until the two components are added to the drain.

- 1 -

COMPOSITION FOR CLEANING DRAINS

The present invention relates to drain cleaner compositions having increased shelf life. Specifically, the invention relates to such compositions wherein one or more components are mixed with a water
5 soluble polymer and formed into beads.

BACKGROUND OF THE INVENTION

Drain lines and other refuse conduits can become clogged when deposits containing food and other material accumulate in various sections of piping, thereby preventing or impeding water from draining properly. Bathroom sinks, tubs and shower drains may similarly
10 become clogged when deposits containing hair accumulate in such areas as the drain sink trap. 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
15 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
20 tested in laboratory simulations. Further, caustic materials are poisonous and can damage many conduit materials and injure people on contact.

Another disadvantage of conventional 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
5 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
10 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
15 methods have led to searches for alternate and better methods of cleaning drain lines clogged with deposits containing hair and/or vegetable matter. One alternative route has involved the use of enzyme-containing compositions. Enzymes can convert common drain clogging
20 materials to water soluble materials which can be removed easily. A potential drawback to their use is that they may have a short shelf life which, in many cases, is attributable to interaction between the various components of the enzyme system. This interaction is
25 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
30 material to expose it to enzymatic action.

There thus remains a need for a drain cleaner which is site specific and which provides, in a single product, a sequential activity of ingredients for enzymatic dissolution of protein such as hair. Further,
35 there is a need for such a drain cleaner product having a

long shelf life even if exposed to high temperatures.

SUMMARY OF THE INVENTION

According to one aspect of the present invention, we provide
5 a formulation for cleaning drains clogged with organic material
deposits which comprises 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 the active ingredient is
10 substantially chemically isolated from any other active
ingredient present in the same bead and the active
ingredient or ingredients in the other beads prior to
dissolution of the polymer. In one embodiment, the
product additionally comprises a liquid component which
15 comprises one or more active drain cleaning ingredients,
wherein the active ingredient(s) in the beads and the
active ingredient(s) in the liquid are kept substantially
chemically isolated from one another until the two
components are added to the drain.

20 DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to drain cleaner
products which are capable of degrading organic
deposits in drain pipes by means of enzymatic action.
The products comprise one or more enzymes and,
25 optionally, additional active ingredients. In one
embodiment of this invention, each active ingredient of
the product is mixed with a melted, water-soluble
polymer, then the mixture is formed into solid, water-
soluble beads or pellets. In an alternative embodiment,
30 two or more active ingredients are contained in the same
beads, provided that the ingredients either are not
interactive or are held in the bead in such a way that
they do not interact. For example, ingredients which

interact in solution may be nonreactive when contained in a solid bead, or the bead may comprise multiple layers which keep the various active ingredients physically separate from one another. The polymer remains intact
5 until it is exposed to water, whereupon it dissolves and releases the active ingredient or ingredients.

In a further embodiment of this invention, the product contains, in addition to one or more types of beads as described above, a second component which is in
10 liquid form. This liquid component comprises one or more active drain cleaning ingredients. In this embodiment of the invention, the bead component and the liquid component are kept substantially physically separate from one another until they are added to the drain. This
15 embodiment will be discussed in greater detail below.

It has been found that mixing active drain cleaning ingredients with a polymer and forming the mixtures into water-soluble beads provides a number of advantages in enzyme-based drain cleaner formulations. Such
20 formulations may contain more than one kind of enzyme, each one specific for a particular type of organic material, so that drain-clogging deposits comprising a variety of substances can be effectively removed. In some cases, however, mixing the enzymes directly is
25 detrimental to shelf life because the enzymes can interact, especially at elevated temperatures. Any additional ingredients can similarly so interact with one another or with the enzymes. By putting individual ingredients into solid beads with a water soluble polymer
30 or by combining two or more ingredients together into beads, such that they cannot substantially chemically interact, any number of enzymes and other ingredients can be included in a single composition without interacting with one another or degrading over time. The shelf life
35 of the product is, therefore, greatly improved.

Another advantage of forming active ingredients into beads is that the drain cleaner becomes site specific. The beads fall through any standing water in the drain and sink to the clog; most, if not all, of the composition reaches the deposit in the drain prior to dissolution of the polymer. Further, since the dissolution time of the polymer is dependent upon the size of the bead and the ratio of polymer to active ingredient in the bead, a sequencing, or ordering, of reactions can be set up. For example, if the enzymes in the composition are active within a particular pH range, a buffering component can be formed into beads which will dissolve more quickly than the beads containing the enzyme. When the polymer in the enzyme beads subsequently dissolves, the enzyme will be released into an environment having a pH at which the enzyme is most active.

In general, there are two types of organic deposits that commonly can clog drain pipes, namely, food and other vegetable matter, and hair. It has been found that products can be made in accordance with this invention which are effective in removing both types of deposits from drains.

Commonly assigned U.S. Patent Application Serial Number 650,510, filed September 14, 1984, discloses enzyme compositions useful for cleaning drains clogged with food and other vegetable material. The enzymes remove these deposits by degrading into small units the polymers associated with the cell walls of the material. Once this has been done, the material blocking the drain line can be dislodged by normal flushing action of the drainage system. Such cell wall polymers include cellulose, pectic substances, hemicelluloses, glycoproteins, and miscellaneous polysaccharides. A more

complete listing of these polymers, and the enzymes which degrade them, is provided in Table 1.

Table 1

Plant Cell Wall Polymers

5	<u>Category of Polymer</u>	<u>Structure (Substrate)</u>	<u>Enzyme</u>
	Cellulose	-4D-glucan	Cellulase
	Pectic Substances	Galacturon rhamnogalacturonan arabinans	Pectinases
10		Galactans and Type I arabinogalactans (linear 1-4D- galactan chains)	
15	Hemicelluloses	Xylans (arabinoxylans and 4-O-methyl glucaronoxylans) Glucomannans and galactoglucomannans	Hemicellu- lases
20		Xyloglucans -D-Glucans (1-3 and 1-4 linkages)	
25	Misc. Polysaccharides	1-3 D-glucans (callose) Type II arabinogalactans (1- 4-D galactan chains which are highly branched via 1-3 and 1-6 galactose linkages) Glucuronomannans	Various polysac- charases
30			
	Glycoproteins	Glycans	Proteases

35 Preferred drain cleaner products for removal of food and/or non-food plant material-containing deposits comprise a mixture of at least one pectinase and at least one cellulase. The pectinases can be either esterases or depolymerases. Depolymerases consist of lyases and hydrolases. Preferred pectinases are derived from

microorganisms of the genus Asperigillus, such as niger or japonicus, or the genus Trichoderma, such as reesei or viride, or the genus Aureobasidium e.g. Aureobasidium pullulans. Preferred cellulases are derived from microorganisms of the genus Thielavia e.g. Thielavia terrestris, the genus Trichoderma e.g. Trichoderma reesei and the
5 genus Sporotrichum e.g. Sporotrichum cellulophilum. It is desirable to maintain these enzymes at a pH in the range of about 3.5 to about 5.5 to enhance their ability to degrade the polymers of the plant cell walls.

10 Commonly assigned U.S. Patent Application Serial Number 485,473, filed April 15, 1983, discloses enzyme compositions useful for cleaning drains clogged with hair and hair-containing deposits. In accordance with the invention of that application, hair-containing deposits
15 can be dissolved by the action of a mixture of a hair disintegrating amount of a proteolytic enzyme and a disulfide reducing agent which are maintained at a pH that enhances hair denaturation. The disulfide reducing agent acts to break the disulfide bonds through which
20 cysteine cross-links hair proteins into a crystalline structure. This 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
25 hydrolyze the peptide bonds of the protein).

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
30 or B. amyloliquefaciens. In addition, an enzyme such as the plant protease papain or an alkaline protease derived from a microorganism of the genus Streptomyces, e.g. Streptomyces griseus, may be used. A single protease or mixture of several different proteases can be used. Disulfide reducing agents include any which function at
35 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 β -mercaptoethanol, may be used.

Highly preferred is sodium thioglycolate.

5 These various enzyme containing products 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 ingredient of the
10 drain cleaning beads of this invention may be a buffer to maintain a pH that enhances hair denaturation or plant cell wall polymer degradation. Other optional additives include detergents, stabilizers, thickening agents and cofactors for the enzymes. The detergents may be anionic
15 or nonionic compounds, including sodium dodecyl sulfate, octyl phenoxypolyethoxyethanol and polyoxyethylene sorbitan mono-oleate. A preferred detergent is sodium dodecyl sulfate. Suitable thickening agents include hydroxy-ethyl cellulose, polyacrylamide and derivatives
20 of xanthan gum. A preferred stabilizer is N,N,N',N'-tetrakis (2-hydroxypropyl)ethylene diamine. Propylene glycol may also be employed as a stabilizer. Cofactors may be included to enhance enzyme activity or their stability once they have been released from the
25 polymer bead at the site of the clog. For example, if one of the enzymes in the composition is a lipase, a lipid solubilizing material can be included as a component to enable the lipase to act more effectively on the fats present in the drain clogging deposit. These
30 various optimal ingredients can be added in amounts sufficient to enhance enzymatic activity.

 The drain cleaner bead formulations of this invention can be specific for hair-containing deposits, for vegetable material-containing deposits, or can contain a
35 mixture of hair-dissolving and vegetable material-degrading enzymes. For the latter, the sequence of bead

dissolution is arranged such that the first beads to dissolve adjust the pH to a level conducive to activity by either the hair-dissolving or vegetable dissolving enzymes. The selected enzyme bead then dissolves and acts on the clog. Beads then dissolve which raise or lower the pH, as required, for proper action by the remaining enzyme, which dissolves last. In this way, the pH level at the clog is optimized at different time intervals for different enzymatic actions.

Alternatively, the different enzymes and buffers can be contained in different layers of the same beads. The outermost layer of the beads would contain the first buffering agent, the second layer would contain the first enzyme to act on the deposit and so on.

A suitable water-soluble polymer is polyethylene glycol (PEG), for example, 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 for disintegrating hair, wherein only one

active ingredient is contained in each bead, about 5 to about 50% of the beads can comprise a mixture of an alkaline protease dispersed in polyethylene glycol, the weight to weight ratio of enzyme to PEG ranging from about 1:1 to about 1:1000, and about 10 to about 95% of the beads can comprise a mixture of a disulfide reducing agent dispersed in PEG, the weight to weight ratio of reducing agent to PEG ranging from about 1:1 to 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. In compositions for degrading vegetable material, the weight to weight ratio of cellulase(s) and pectinase(s) to polymer can range from about 1:1 to about 1:500.

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 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 ingredients to be mixed with the polymer 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.

As noted previously, in a further embodiment of this invention, the drain cleaning product may comprise in
5 addition to its solid bead component a liquid component which also comprises one or more active drain cleaning ingredients. Typically, the liquid component and solid bead component are kept physically isolated from one another until the product is used to prevent premature
10 degradation of the polymer coated beads.

The liquid component of the liquid/solid drain cleaner product may comprise one or more active ingredients which do not have a short shelf life and will not substantially interact with other ingredients in the
15 liquid. This liquid/solid formulation may be specific for hair-containing deposits, for vegetable material-containing deposits or for deposits containing a combination of material.

For example, in the drain cleaner formulation for
20 opening drains clogged with a hair containing deposit discussed above, which comprises a protease and a disulfide reducing agent maintained at a pH that enhances hair denaturation, the protease advantageously is mixed with a polymer and formed into beads to enhance its
25 stability during storage. The disulfide reducing agent, rather than also being in bead form, as discussed above, may be in an aqueous solution. The disulfide reducing agent may be any of those set forth above. A preferred disulfide reducing agent in this embodiment of the appli-
30 cation is ammonium thioglycolate. An advantage to using the ammonium salt, rather than the sodium salt, of thioglycolic acid is that the ammonium thioglycolate is non-caustic. Additionally, the presence of ammonium thioglycolate in the drain can provide a pH environment

in the drain that enhances hair denaturation without the need for additional buffers.

In this embodiment, the disulfide reducing agent can be provided simply by mixing ammonium hydroxide with
5 thioglycolic acid. The concentration of the ammonium thioglycolate can range from about 30-35% to about 1%, depending upon the amount used. Sufficient ammonium thioglycolate is needed to break the disulfide bonds of the hair. Preferably, the reducing agent is provided in
10 fairly concentrated form, so that when added to the drain, it will sink through standing water that may be present and reach the deposit. The enzyme-containing beads are produced as described above, and the weight to weight ratio of enzyme to reducing agent typically
15 remains within the ratio of about 1:1 to about 1:200.

In this example of the liquid/solid formulation, the enzyme-containing bead component preferably also may comprise an alkali metal bisulfite compound. As disclosed in co-pending, commonly assigned U.S. patent
20 application S.N. 681,636, filed December 14, 1984, and incorporated herein by reference, the addition of an alkali metal bisulfite compound, within certain concentrations, appears to modify the proteolytic enzyme(s) of the formulation such that their rate of
25 activity is enhanced. Generally, the amount of bisulfite added is within the range of about 0.001 to about 0.1 weight percent of the total formulation. The weight to weight ratio of bisulfite compound to enzyme generally ranges from about 1:10 to about 1:1000 and preferably
30 ranges from about 1:50 to about 1:500. A preferred bisulfite compound is sodium bisulfite.

To dissolve a hair-containing deposit in a drain using this liquid/solid formulation, the enzyme-containing bead product typically is added to the drain
35 first, followed by the disulfide reducing agent-

containing liquid. By adding the products in this order, the enzyme-containing beads can begin to dissolve while the disulfide reducing agent softens the hair. Once the disulfide bonds in the hair have been broken, the

5 proteolytic enzyme will be available to break the covalent bonds of the hair protein and effectively disintegrate the hair. Prior to adding the liquid/solid formulation to the drain, the liquid and solid

10 components typically are kept physically separate from one another, as in separate containers or packages, to avoid premature dissolution of the enzyme beads.

The following examples illustrate how a multi-component drain cleaner product made in accordance with this invention can be made and the effectiveness of such

15 a composition.

Example I

A drain cleaner bead product was prepared having three different types of polymer-encapsulated active ingredients: sodium dodecylsulfate (SDS), a high

20 alkaline protease (obtained from Enzyme Development Corporation), and sodium thioglycolate (Na-TGA). The polymer used was polyethylene glycol (Fisher Brand PEG8000). The beads were produced by extruding a mixture of the active ingredient and the polymer through a

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

TABLE II

Bead Production Parameters

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

* PEG₈₀₀₀ lab source - Fisher; Commercial Source -
BASF Wyandotte

15 ** 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
20 plate (non-stirring). A Pharmacia K16 column was
connected to a heating water bath and the temperature
adjusted accordingly (see Table II). The active
component was then added to the PEG and mixed well. In
the case of enzyme beads, the enzyme solution was added
25 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. In the case
of SDS beads, the mixture was stirred gently to avoid
30 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
35 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 II). 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

Beads produced by the general procedure as described in Example I were used for hair degradation tests in test tubes. To each of 5 test tubes 2 grams of dry hair was packed into the bottom and 50 ml of water was added. To this 5 grams of the beaded product as produced in Example I were added. The product consisted of 1.56 gm

of enzyme beads, 0.78 gm of SDS beads and 3.52 gm of TGA beads. The beads were added to the test tube and allowed to sit unstirred for 16 hours. At this time the hair was observed to have undergone significant degradation. The hair from each test tube was removed, washed, dried and weighed to determine the total amount of degradation. The degradation in test tubes 1-5 was 91.7, 86.2, 85.1, 80.3 and 82.7%, respectively, for an average of 86.0% degradation. This represents 1.72 grams of hair that was totally degraded.

Example III

Beads produced by the general method as described in Example 1 were added to a hair clogged test drain trap. For this test 15 grams of dry hair was packed into the trap portion of the drain and 10 g of drain cleaner beads were applied to the drain trap which contained water. The application was 5 times the amount added in Example 2 but represented a lower proportion of cleaner to hair as the hair was 7.5 time as great. After overnight treatment (approximately 16 hours) the drains were flushed with water whereupon the clog dislodged and a clear drain resulted. The hair was collected, washed, dried and weighed. There was a 57.7% degradation of the original hair as calculated from that remaining in the drain after overnight treatment.

Example IV

The general procedure of Example 3 was followed and the amount of hair that degraded after overnight treatment was 62.6% as calculated from the amount of hair that was flushed from the previously clogged drain.

Example V

An application (10 grams) of the solid drain cleaner was used to clear a slow-running drain in a home whereupon it was presumed that the major cause of the clog was hair. The drain was tested for water flow (9 liters) before and after the treatment. The treatment lasted 3.25 hours. The flow times are listed in Table II. There was a decrease in total time of flow attributed to the treatment and the drain was no longer slow running.

TABLE III

	<u>Water Flow Before (Seconds)</u>	<u>Water Flow After (Seconds)</u>
Trial 1	37	23
15 Trial 2	36	20
Trial 3	40	22
Average	38	22

Example VI

A drain cleaner bead product can be made wherein the beads contain all of the active ingredients, each found within a separate layer of the beads.

Core beads are made as described in Example I comprising polyethylene glycol and TGA. A separate mixture is made of the polyethylene glycol and SDS. The core beads are dipped in this solution for a period of time sufficient to coat the beads with the liquid SDS-PEG mixture but insufficient to cause the beads to melt. The coated beads then are withdrawn and cooled to allow the coating to solidify. This procedure can be repeated as many times as necessary to coat the core beads with the desired amount of SDS. The dipping, coating and cooling

process then is repeated with the two-layer beads and a liquid mixture of the proteolytic enzyme and PEG. When adding the enzyme-PEG layer to the beads it is desirable to quickly cool the coated beads so as to minimize any enzyme thermal deactivation.

Other approaches can be used to produce multi-layered beads. The core beads can comprise the enzyme-PEG mixture and be coated with TGA and with SDS. As shown in Example I, the enzyme and PEG typically can be mixed at a lower temperature than can the TGA or SDS and PEG. If the enzyme-PEG mixture is the core bead, care must be taken so that the core bead does not melt when the other bead layers are formed, such as by cooling the beads before dipping them in the melted TGA- or SDS-PEG mixtures.

Example VII

Pre-polymer solutions were made as in Example I, with the exception that the TGA and SDS prepolymers were made at 70°C and the enzyme prepolymer was made at 55°C. All three solutions were mixed together to form a uniform solution. Beads containing all three components were then made according to the general procedure as described in example I.

Five grams of the beads were added to a test tube containing two grams of hair and 50 ml. of water and allowed to sit undisturbed for 22 hours. At this time the hair was observed to have undergone significant degradation. The hair was removed from the test tube, washed, dried, and weighed. Only 0.829 g. of hair remained (58.6% of the hair had been degraded).

Example VIIIPreparation of Liquid/Solid
Drain Cleaner Formulation

Ammonium hydroxide (29.2ml) was added to 12.5ml of
5 cooled thioglycolic acid along with 0.69ml of lavender
scent and mixed well. This solution was poured into a
graduated cylinder and the volume was brought up to 60ml
with diH₂O. This solution plus 7.8gm of enzyme beads
constituted a single application of liquid/solid drain
10 cleaner. The enzyme beads were made according to the
general procedure described in Example I, with the
exception that sodium bisulfite (SBS) was added to the
enzyme solution before it was mixed with the PEG.
Sufficient SBS was added that the liquid pre-polymer
15 contained 0.05% SBS.

Example IX

Twenty grams of hair and one gram of a calcium soap
curd were mixed and packed into each of five drain
traps. One liter of water was poured through the drain
20 and the flow rate determined.

An application of the liquid/solid drain cleaner
formulation (0.4 oz. enzyme beads, 2 oz. ammonium
thioglycolate) prepared in Example VIII was added to each
drain. The enzyme beads were added first, followed by
25 the ammonium thioglycolate. After 8 hours the drains
were flushed with one liter of water. Hair was collected
from each trap and filtered through a 125 micron sieve.
All the insolubles were collected, dried and weighed.

The results are shown in Table 4 below. A cleared
30 drain indicated that all hair was dislodged from the
drain trap.

Table 4
Effectiveness of (20.8% TGA) Liquid/Solid Drain
Cleaner on Hair Degradation

5	Drain I.D. #	Before Treatment	Results of the Treatment	Grams of	
				Hair Degraded	% Hair Degraded
10	1	1 min. 10 sec.	drain cleared	16.1	80.5
	2	2 min. 24 sec.	drain cleared	11.35	56.8
	3	2 min. 33 sec.	drain cleared	9.46	47.3
	4	1 min. 41 sec.	drain cleared	11.43	57.2
	5	1 min. 15 sec.	drain cleared	13.32	66.6

CLAIMS:

1. A formulation for cleaning drains clogged with organic deposits, comprising:
a plurality of water-soluble beads, wherein
5 each bead comprises a mixture of at least one active drain cleaning ingredient dispersed in a water-soluble polymer such that the active ingredient is substantially chemically isolated from any other active ingredient present in the same bead and
10 the active ingredient or ingredients in the other beads.
2. A formulation as claimed in claim 1 wherein each bead comprises a mixture of at least one active ingredient selected from enzymes, detergents,
15 buffers, reducing agents, enzyme cofactors, thickening agents and stabilizers dispersed in a water-soluble polymer.
3. A formulation as claimed in claim 1 or claim 2 wherein each bead comprises only one active ingredient.
- 20 4. A formulation as claimed in claim 1 or claim 2 wherein at least some of the beads contain two or more active drain cleaning ingredients and are formed such that they comprise multiple layers, each layer comprising only one active ingredient.
- 25 5. A formulation as claimed in claim 1 or claim 2 wherein at least some of the beads contain two or more active ingredients, each of which is dispersed uniformly throughout the beads.
6. A formulation as claimed in any one of claims 1
30 to 5 wherein the water-soluble polymer is polyethylene glycol.
7. A formulation as claimed in any one of the preceding claims which comprises, in addition to a solid component comprising a plurality of beads,
35 a liquid component which comprises one or more active drain-cleaning ingredients, the active ingredient(s) in the beads and the active ingredient(s)

in the liquid being kept substantially chemically isolated from one another until the two components are added to the drain.

8. A formulation as claimed in any one of claims 1 to 7 for cleaning drains clogged with a hair-containing deposit wherein the active ingredients of the water-soluble beads comprise at least one proteolytic enzyme and a disulfide-reducing agent.

9. A formulation as claimed in claim 7 for cleaning drains clogged with a hair-containing deposit which comprises a plurality of water-soluble beads comprising a mixture of at least one proteolytic enzyme dispersed in a water-soluble polymer and a liquid component comprising a disulfide-reducing agent.

10. A formulation as claimed in claim 8 or claim 9 wherein the disulfide-reducing agent is selected from the group consisting of calcium thioglycolate, ammonium thioglycolate, potassium thioglycolate and sodium thioglycolate.

11. A formulation as claimed in claim 8 or claim 9 wherein the disulfide-reducing agent is β -mercapto-ethanol.

12. A formulation as claimed in claim 10 which comprises:

a plurality of water-soluble beads wherein about 5% to about 50% of the beads comprise a mixture of an alkaline protease dispersed in polyethylene glycol (PEG), the weight to weight ratio of enzyme to PEG ranging from about 1:1 to about 1:1000; and about 10 to about 95% of the beads comprise a mixture of sodium thioglycolate dispersed in polyethylene glycol, the weight to weight ratio of sodium thioglycolate to PEG ranging from about 1:1 to about 1:1000.

13. A formulation as claimed in claim 10 which comprises:

a plurality of water-soluble beads wherein about 5% to about 50% of the beads comprise a mixture of an alkaline protease dispersed in polyethylene

- glycol (PEG), the weight to weight ratio of enzyme to PEG ranging from about 1:1 to about 1:1000; and about 10 to about 95% of the beads comprise a mixture of sodium thioglycolate dispersed in polyethylene glycol, the weight to weight ratio of sodium thioglycolate to PEG ranging from about 1:1 to about 1:1000; and about 0.1% to about 20% of the beads comprise a mixture of sodium dodecylsulfate (SDS) dispersed in PEG, the weight to weight ratio of SDS to PEG ranging from about 1:1 to about 1:1000.
14. A formulation as claimed in any one of claims 9 to 11 having liquid component comprising a disulfide-reducing agent wherein the water-soluble, proteolytic enzyme-containing beads additionally comprise an alkali metal bisulfite compound.
15. A formulation as claimed in any one of claims 1 to 6 for cleaning drains clogged with food and/or non-food plant material-containing deposits wherein the active ingredients of the water-soluble beads comprise at least one pectinase and at least one cellulase.
16. A formulation as claimed in claim 15 wherein the active ingredients of the water-soluble beads additionally comprise one or more enzymes selected from hemicellulases, polysaccharases, proteases and lipases.
17. A formulation as claimed in any one of claims 8 to 16 which also comprises at least one additional ingredient selected from buffers, detergents, stabilizers, thickening agents and enzyme cofactors
18. A method for cleaning a drain clogged with an organic deposit which comprises contacting the deposit with an effective amount of a formulation as claimed in claim 1.
19. A method for cleaning a drain clogged with an organic deposit which comprises contacting the deposit with an effective amount of a formulation as claimed in any one of claims 3 to 5.

20. A method for cleaning a drain clogged with an organic deposit which comprises contacting the deposit with an effective amount of a formulation as claimed in claim 7.

5 21. A method for cleaning a drain clogged with a hair-containing deposit which comprises contacting the deposit with an effective amount of a formulation as claimed in claim 8.

22. A method for cleaning a drain clogged with
10 a hair-containing deposit which comprises contacting the deposit with an effective amount of a formulation as claimed in claim 14.

23. A method for cleaning a drain clogged with a food and/or non-food plant material-containing
15 deposit which comprises contacting the deposit with an effective amount of a formulation as claimed in claim 15.



European Patent
Office

EUROPEAN SEARCH REPORT

0178931

EP 85 30 7500

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int Cl 4)
P, A	EP-A-0 125 801 (GENEX CORP.) * claims 1-5, 11 *		C 11 D 3/386 C 11 D 17/00
A	US-A-3 506 582 (D.P. GERTZMAN) * abstract, claims 1, 5 *		
A	CH-A- 493 630 (MONSANTO CO.) * claim 1 *		
			TECHNICAL FIELDS SEARCHED (Int Cl 4)
			C 11 D 3/00 C 11 D 17/00
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 20-12-1985	Examiner SCHULTZE D
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : member of the same patent family, corresponding document	