



(86) Date de dépôt PCT/PCT Filing Date: 1999/11/16
(87) Date publication PCT/PCT Publication Date: 2000/05/25
(45) Date de délivrance/Issue Date: 2006/03/21
(85) Entrée phase nationale/National Entry: 2001/04/26
(86) N° demande PCT/PCT Application No.: US 1999/027200
(87) N° publication PCT/PCT Publication No.: 2000/029535
(30) Priorité/Priority: 1998/11/16 (60/108,547) US

(51) Cl.Int./Int.Cl. *C11D 3/386* (2006.01),
C11D 7/54 (2006.01), *C11D 7/42* (2006.01),
B08B 3/12 (2006.01), *C11D 3/395* (2006.01)

(72) Inventeurs/Inventors:
MCKENZIE, KRISTEN LYNNE, US;
SCHEPER, WILLIAM MICHAEL, US;
THOEN, CHRISTIAAN ARTHUR JACQUES KAMIEL,
US;
KASTURI, CHANDRIKA, US

(73) Propriétaire/Owner:
THE PROCTER & GAMBLE COMPANY, US

(74) Agent: KIRBY EADES GALE BAKER

(54) Titre : PRODUIT DE NETTOYAGE A ONDES SONORES OU ULTRASONORES
(54) Title: CLEANING PRODUCT WHICH USES SONIC OR ULTRASONIC WAVES

(57) **Abrégé/Abstract:**

The present invention relates to compositions, product kits, devices and processes for cleaning using sonic or ultrasonic waves with ultrasonically enhanced cleaning agents. The product and process of the present invention can be used as a hand dishwashing composition, a hard surface cleaner, an automatic dishwashing composition and the like.



ABSTRACT

The present invention relates to compositions, product kits, devices and processes for cleaning using sonic or ultrasonic waves with ultrasonically enhanced cleaning agents. The product and process of the present invention can be used as a hand dishwashing composition, a hard surface cleaner, an automatic dishwashing composition and the like.

CLEANING PRODUCT WHICH USES SONIC OR ULTRASONIC WAVES

FIELD OF THE INVENTION

The present invention generally relates to compositions, product kits, devices and processes for cleaning using sonic or ultrasonic waves.

BACKGROUND OF THE INVENTION

Ultrasonic cleaning is a well known cleaning process in industry. For example, it is used to clean electronic components after or during immersion in cleaning solution such as azeotropic mixtures of fluoro hydrocarbons. It is also used domestically to a small extent in oral hygiene, as in ultrasonic tooth brushes. However, ultrasonic cleaning has not found much acceptance domestically beyond this limited application.

While ultrasonics do give good cleaning in these limited applications there has been no truly breakthrough cleaning performance from the combination of ultrasonic or sonic energy with conventional cleaning additives. Many and varied combinations have been tried resulting in either insignificant cleaning benefits or additional problems which make any benefits impracticable.

Accordingly there remains in the art the search for a cleaning ingredient or ingredients which will provide surprisingly and unexpected superior cleaning when used in conjunction with ultrasonic or sonic energy.

BACKGROUND ART

US 5,464,477, US 5,529,788, US 4,308,229, US 4,448,750; WO 94/07989, WO 97/16263, WO 94/23852, WO 93/06947; GB 2,204,321; EP 258,819; DE 4,100,682; JP 10036892, JP 08157888.

SUMMARY OF THE INVENTION

It has now been surprisingly found that certain specific ingredient or ingredients which will provide surprisingly and unexpected superior cleaning when used in conjunction with ultrasonic or sonic energy. These cleaning ingredients are called ultrasonically enhanced cleaning agents and are selected from bleach catalysts, amylase enzymes and mixtures thereof.

The present invention also includes ultrasonic cleaning products which comprise:

- (a) a cleaning composition comprising an ultrasonically enhanced cleaning agent which is a bleach catalyst; and
- (b) a sonic or ultrasonic wave generating source for imparting sonic or ultrasonic waves, said sonic or ultrasonic wave generating source including a transducer wherein said transducer oscillates at a frequency of from about 100 Hz to about 20,000 Hz.

The present invention also comprises a process for removing tough food from a hard surface comprising the steps of:

- (i) applying an effective amount of a cleaning composition to said tough food on said hard surface, said cleaning composition comprises an ultrasonically enhanced cleaning agent which is a bleach catalyst; and
- (ii) imparting sonic or ultrasonic waves to said tough food so as to remove said tough food from said hard surface.

As used herein, the phrase "ultrasonic waves" means mechanical pressure or stress waves which can propagate through any material media, wherein the frequency spectra of these waves can vary from a few cycles/second (Hz) to a few billion Hz.

All percentages, ratios and proportions herein are by weight, unless otherwise specified.

BRIEF DESCRIPTION OF THE DRAWING

FIGURE 1 is a perspective view of a hand-held, ultrasonic device, with a cleaning solution storage means which is adapted to be removably mounted in the device. Also shown are a removably mountable cleaning head and an additional cleaning solution storage means.

FIGURE 2 is a perspective view of two different hand-held, pen-shaped ultrasonic devices, which are used in the invention to impart ultrasonic waves onto a stain or soil.

FIGURE 3 is a perspective view of a hand-held, pen-shaped ultrasonic device, which is shown imparting ultrasonic waves onto a soil.

FIGURE 4 is a perspective an ultrasonic device, which are used in the invention to impart ultrasonic waves onto a stain or soil. The ultrasonic generator and the power

source are in a second housing which is associated with the cleaning head which is in a first housing.

DETAILED DESCRIPTION OF THE INVENTION

As it was stated previously, the present invention also includes ultrasonic cleaning products which comprise:

- (a) a cleaning composition, preferably a liquid or gel, comprising an ultrasonically enhanced cleaning agent selected from the group consisting of amylase enzyme, bleach catalyst and mixtures thereof; and
- (b) a sonic or ultrasonic wave generating source for imparting sonic or ultrasonic waves.

Preferably the ultrasonically enhanced cleaning agents is present in the cleaning composition in an effective amount, more preferably from about 0.0001% to about 40%, even more preferably from about 0.001% to about 20%, even more preferably still from about 0.005% to about 10%, even more preferably still from about 0.01% to about 5% by weight. It has been surprisingly found that these ultrasonically enhanced cleaning agents deliver increased cleaning performance when they are used in cleaning in conjunction with ultrasonic or sonic energy. These cleaning compositions can comprise additional cleaning additives and these are exemplified in greater detail hereafter.

In another aspect the cleaning composition can be a hand dishwashing composition (a so called LDL), a hard surface cleaner, an automatic dishwashing composition. Alternatively the cleaning composition could be a composition specifically formulated for use in ultrasonic cleaning, so called UCC or ultrasonic cleaning compositions. Furthermore, the cleaning composition could be just an ultrasonically enhanced cleaning agent alone or with one or more conventional cleaning agents which do not resemble any of these conventional cleaning compositions mentioned previously.

The cleaning composition in the ultrasonic cleaning products can be, for example, in a storage means in the ultrasonic device, in another container in the same product and designed to be added to the storage means in the ultrasonic device before use, in another container in the same product and directly added to the surface to be cleaned, in another container in the same product and made into an aqueous solution in which the surface is immersed, in another container in the same product and applied to by the user from

another container to the cleaning surface of the ultrasonic device either neat or as an aqueous solution, or in another container in the same product as an aqueous solution. These are merely some possible examples and not intended to be limiting.

In one aspect the ultrasonically enhanced cleaning agent is a bleach catalyst and is preferably selected from the group consisting of manganese bleach catalysts, cobalt bleach catalysts, iron bleach catalysts and mixtures thereof.

It is believed that, while not wanting to be limited by theory, that the ultrasonic energy improves the rehydration of the soil and hence makes it easier to clean. It is believed to do this by increasing the surface area of the emulsion by either forming cracks or increasing the size of cracks already present, in the soil. This gives the cleaning solution a greater surface area to rehydrate the soil.

By using this composition with a source of ultrasonic energy, stains or tough soils can be removed without the use of excessive force, rubbing, pressure or other manipulation which causes wear and tear on the stained material or surface. In doing so, the user does not need to impart such manual energy to remove the stain, thereby adding to the convenience of the user. The invention also encompasses processes by which such stains or soils are removed, either from localized regions or from the entire article to be cleaned.

The present application also includes methods of washing tableware and hard surfaces by either applying a neat or aqueous solution to the soil or stain, to be removed from the surface and the imparting ultrasonic or sonic waves to the soil or stain. Furthermore, the present application also includes methods of washing tableware by contacting the tableware with an aqueous solution, such as by immersion in an aqueous solution, then imparting sonic or ultrasonic waves to said soiled tableware. It is preferred that the surface be a hard surface. A "hard surface" is any surface which is traditionally regarded as hard, that is tableware, such as plates, glasses, cutlery, pots and pans, and also includes other surfaces such as kitchen counter tops, sinks, glass, windows, enamel surfaces, metal surfaces, tiles, bathtubs, floors etc. More preferably, the hard surface is tableware.

It is preferred that these ultrasonic cleaning products further comprise instructions for using the product. One preferred set of instructions comprises the steps of

- (i) applying an effective amount of said cleaning composition to said surface;
- (ii) imparting sonic or ultrasonic waves to said surface using said device; and
- (iii) optionally, rinsing the surface with an aqueous solution.

Another, preferred set of instructions comprise the steps of:

- (i) using said device to apply an effective amount of said cleaning composition to said surface concurrently and coterminous with said cleaning head;
- (ii) moving said cleaning head over and maintain contact thereto said surface and
- (iii) optionally, rinsing the surface with an aqueous solution.

As it was stated previously, The present invention also comprises a process for removing tough food from a hard surface comprising the steps of:

- (i) applying an effective amount of a cleaning composition to said tough food on said hard surface, said cleaning composition comprises an ultrasonically enhanced cleaning agent selected from the group consisting of amylase enzyme, bleach catalyst and mixtures thereof; and
- (ii) imparting sonic or ultrasonic waves to said tough food so as to remove said tough food from said hard surface; and
- (iii) optionally, rinsing said hard surface with an aqueous solution.

In one aspect of this it is preferred that steps (i) and (ii) are conducted simultaneously using a device that permits controlled dispensing of said liquid cleaning composition to the stain while concurrently imparting sonic or ultrasonic waves thereto.

The source of ultrasonic or sonic energy or waves can be from any suitable source. A variety of sonic or ultrasonic sources can be used in the invention including, but not limited to, sonic cleaning baths typically used to clean jewelry and sonic toothbrushes for cleaning teeth. This includes basins or sinks, such as the Branson™ Ultrasonic Bath, ultrasonic "balls", which are dropped into a conventional sink or basin, such as the Sonic Wash Ball™ by "D&P Wash Machine", baskets or racks into which the item to be cleaned is placed and this is then placed into a conventional sink or basin. Alternatively, the source of ultrasonic energy could be provided by a modified ultrasonic tooth brush, such as the Teledyne Water Pik™ model SR-400R. It is one preferred aspect that sonic or ultrasonic source is a, hand-held vibrational ultrasonic device with a cleaning head one distal end of said device. It is another preferred aspect that in

ultrasonic cleaning product the cleaning composition and the sonic or ultrasonic source contained in together in a device that permits controlled dispensing of the cleaning composition to a hard surface in need of cleaning, while concurrently imparting sonic or ultrasonic waves thereto.

In one aspect of the present invention the acoustic system, which generates the sonic or ultrasonic waves is made from a piezo ceramic element or elements, typically called PZTs, along with an acoustic amplifier, typically called an acoustic horn or acoustic transducer or sonotrode. The entire acoustic system is designed to operate at a specific frequency and power and deliver a predetermined amplitude at the end or tip of the sonotrode. The combination of the sonotrode design, amplitude, frequency and power dictates the cleaning efficacy. Further, not all of the parameters are independently chosen.

With regards to the design of the sonotrode, a variety of different shapes provide improved cleaning benefits. One specific embodiment is a "chisel" design, where the sonotrode is tapered at the end which will contact, or be proximate to, the stain/soil to be removed. Typically, the width of the sonotrode is much less than its length. For example the sonotrode may be 0.05 to 5 mm wide and the is 10 to 50 mm long. In one embodiment, cleaning is improved when the sonotrode is designed to deliver equal amplitude across the sonotrode blade. However, there are other embodiments where having a higher localized amplitude is preferred. In one embodiment, it has surprisingly been found that a sonotrode blade in a "chisel" shape running at 50kHz, 30 Watts and 40 microns provides significant cleaning benefits.

In another embodiment, it has surprisingly been found that sonotrodes designed in a "disc" or round shape deliver significant cleaning benefits. This sonotrode embodiment typically has a disc radius of from 10 to about 100 mm. Further, the sonotrode may present a more three dimensional appearance to the stain/soil to be cleaned. The sonotrode may be in the shape of a hemisphere or may be disc shaped with undulations or dimples on the surface. In another embodiment, the sonotrode can be rectangular, oval, triangular shaped. Because of ergonomic considerations, it is preferred that the sonotrode have rounded edges. Each of these different embodiments offers unique cleaning opportunities. In addition, the mass of the sonotrode is important to achieve the

desired cleaning benefit. It has surprisingly been found that the sonotrode must have a mass between 20 and 500 grams.

Further, the sonotrode material must be chosen to have the desired acoustic properties and also be compatible with the chemistry being used in the cleaning application. Suitable materials include titanium, aluminum and steel, preferably hardened steel. Less preferred, but acceptable for cleaners which are substantially free from bleaches and alkalinity is aluminum.

In another aspect of the present invention the acoustic system and in particular the sonotrode may be encased, surrounded, or in close proximity to adjunct materials to aid in the cleaning process. These include, but are not limited to, sponges, scouring pads, steel wool pads, high friction non-wovens, and absorbent natural and synthetic materials. These adjunct materials can help cleaning by removing the soils and stains that are loosened by the ultrasonic plus chemistry, and/or they can act to absorb residual stains and/or hold the cleaning solution in close contact with the stain or soil which is in contact with the ultrasonic energy. Optionally, these adjunct pads can be removable and/or disposable.

The transducer means oscillates at a frequency of from about 100 Hz to about 20,000 kHz, more preferably from about 100 Hz to about 10,000 kHz, more preferably from about 150 Hz to about 2000 kHz, more preferably from about 150 Hz to about 1,000 kHz, more preferably from about 150 Hz to about 100 kHz, more preferably from about 200 Hz to about 50 kHz. It is preferred that the average frequency be from about 1000 Hz to about 100kHz, more preferably from about 10,000 Hz to about 70kHz. It is also preferred that the device provides a power output per unit of surface area of said cleaning head of at least about 0.02 watts/cm², more preferably at least about 0.05 watts/cm², even more preferably at least about 0.07 watts/cm², even more preferably still at least about 0.08 watts/cm².

Typical treatment times range from about 1 second to about 5 minutes, more typically from about 20 seconds to about 2 minutes, and most typically from about 30 seconds to 1 minute, although treatment times will vary with the severity of the stain or

toughness of the soil. The sonic or ultrasonic source device can be a vibrational sonic or ultrasonic generator, a torsional sonic or ultrasonic wave generator, or an axial sonic or ultrasonic generator in that it is the shock waves generated by these sonic or ultrasonic sources that does the actual cleaning or loosening of the stain on the textile regardless of the mechanism by which the sonic or ultrasonic shock waves are generated. The sonic or ultrasonic wave generating device can be battery operated or a plug-in type.

Cleaning Compositions -

The compositions herein include one or more ultrasonically enhanced cleaning agents. It is preferred that the compositions further contain one or more conventional cleaning agents for assisting or enhancing cleaning performance, treatment of the substrate to be cleaned, or to modify the aesthetics of the detergent composition (e.g., perfumes, colorants, dyes, etc.). The following are illustrative examples of such adjunct materials.

Ultrasonically Enhanced Cleaning Agent - these are selected from amylase enzymes, bleach catalysts and mixtures thereof. These ultrasonically enhanced cleaning agents may optionally be combined with one or more conventional cleaning additives.

Amylase - Amylases (α and/or β) can be included for removal of carbohydrate-based stains. Suitable amylases are Termamyl® (Novo Nordisk), Fungamyl® and BAN® (Novo Nordisk). The enzymes may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Amylase enzymes are normally incorporated in the detergent composition at levels from 0.0001% to 2%, preferably from about 0.0001% to about 0.5%, more preferably from about 0.0005% to about 0.1%, even more preferably from about 0.001% to about 0.05% of active enzyme by weight of the detergent composition.

Amylase enzymes also include those described in WO95/26397 and WO96/23873. Other specific amylase enzymes for use in the detergent compositions of the present invention therefore include :
 (a) α -amylases characterised by having a specific activity at least 25% higher than the specific activity of Termamyl® at a temperature range of 25°C to 55°C and at a pH value

in the range of 8 to 10, measured by the Phadebas[®] α -amylase activity assay. Such Phadebas[®] α -amylase activity assay is described at pages 9-10, WO95/26397.

(b) α -amylases according (a) comprising the amino sequence shown in the SEQ ID listings in the above cited reference. or an α -amylase being at least 80% homologous with the amino acid sequence shown in the SEQ ID listing.

(c) α -amylases according (a) obtained from an alkalophilic *Bacillus* species, comprising the following amino sequence in the N-terminal : His-His-Asn-Gly-Thr-Asn-Gly-Thr-Met-Met-Gln-Tyr-Phe-Glu-Trp-Tyr-Leu-Pro-Asn-Asp.

A polypeptide is considered to be X% homologous to the parent amylase if a comparison of the respective amino acid sequences, performed via algorithms, such as the one described by Lipman and Pearson in Science 227, 1985, p. 1435, reveals an identity of X%

(d) α -amylases according (a-c) wherein the α -amylase is obtainable from an alkalophilic *Bacillus* species; and in particular, from any of the strains NCIB 12289, NCIB 12512, NCIB 12513 and DSM 935.

In the context of the present invention, the term "obtainable from" is intended not only to indicate an amylase produced by a *Bacillus* strain but also an amylase encoded by a DNA sequence isolated from such a *Bacillus* strain and produced in an host organism transformed with said DNA sequence.

(e) α -amylase showing positive immunological cross-reactivity with antibodies raised against an α -amylase having an amino acid sequence corresponding respectively to those α -amylases in (a-d).

(f) Variants of the following parent α -amylases which (i) have one of the amino acid sequences shown in corresponding respectively to those α -amylases in (a-e), or (ii) displays at least 80% homology with one or more of said amino acid sequences, and/or displays immunological cross-reactivity with an antibody raised against an α -amylase having one of said amino acid sequences, and/or is encoded by a DNA sequence which hybridizes with the same probe as a DNA sequence encoding an α -amylase having one of said amino acid sequence; in which variants :

1. at least one amino acid residue of said parent α -amylase has been deleted; and/or
2. at least one amino acid residue of said parent α -amylase has been replaced by a different amino acid residue; and/or
3. at least one amino acid residue has been inserted relative to said parent α -amylase;

said variant having an α -amylase activity and exhibiting at least one of the following properties relative to said parent α -amylase : increased thermostability, increased stability towards oxidation, reduced Ca ion dependency, increased stability and/or α -amylolytic activity at neutral to relatively high pH values, increased α -amylolytic activity at relatively high temperature and increase or decrease of the isoelectric point (pI) so as to better match the pI value for α -amylase variant to the pH of the medium.

Said variants are described in WO96/23873.

Other amylases suitable herein include, for example, α -amylases described in GB 1,296,839 to Novo; RAPIDASE®, International Bio-Synthetics, Inc. and TERMAMYL®, Novo. FUNGAMYL® from Novo is especially useful. Engineering of enzymes for improved stability, e.g., oxidative stability, is known. See, for example J. Biological Chem., Vol. 260, No. 11, June 1985, pp. 6518-6521. Certain preferred embodiments of the present compositions can make use of amylases having improved stability in detergents such as automatic dishwashing types, especially improved oxidative stability as measured against a reference-point of TERMAMYL® in commercial use in 1993. These preferred amylases herein share the characteristic of being "stability-enhanced" amylases, characterized, at a minimum, by a measurable improvement in one or more of: oxidative stability, e.g., to hydrogen peroxide/tetraacetylenediamine in buffered solution at pH 9-10; thermal stability, e.g., at common wash temperatures such as about 60°C; or alkaline stability, e.g., at a pH from about 8 to about 11, measured versus the above-identified reference-point amylase. Stability can be measured using any of the art-disclosed technical tests. See, for example, references disclosed in WO 9402597. Stability-enhanced amylases can be obtained from

Novo or from Genencor International. One class of highly preferred amylases herein have the commonality of being derived using site-directed mutagenesis from one or more of the *Bacillus* amylases, especially the *Bacillus* α -amylases, regardless of whether one, two or multiple amylase strains are the immediate precursors. Oxidative stability-enhanced amylases vs. the above-identified reference amylase are preferred for use, especially in bleaching, more preferably oxygen bleaching, as distinct from chlorine bleaching, detergent compositions herein. Such preferred amylases include (a) an amylase according to WO 9402597, Novo, Feb. 3, 1994, as further illustrated by a mutant in which substitution is made, using alanine or threonine, preferably threonine, of the methionine residue located in position 197 of the *B. licheniformis* α -amylase, known as TERMAMYL[®], or the homologous position variation of a similar parent amylase, such as *B. amyloliquefaciens*, *B. subtilis*, or *B. stearothermophilus*; (b) stability-enhanced amylases as described by Genencor International in a paper entitled "Oxidatively Resistant α -Amylases" presented at the 207th American Chemical Society National Meeting, March 13-17 1994, by C. Mitchinson. Therein it was noted that bleaches in automatic dishwashing detergents inactivate α -amylases but that improved oxidative stability amylases have been made by Genencor from *B. licheniformis* NCIB8061. Methionine (Met) was identified as the most likely residue to be modified. Met was substituted, one at a time, in positions 8, 15, 197, 256, 304, 366 and 438 leading to specific mutants, particularly important being M197L and M197T with the M197T variant being the most stable expressed variant. Stability was measured in CASCADE[®] and SUNLIGHT[®]; (c) particularly preferred amylases herein include amylase variants having additional modification in the immediate parent as described in WO 9510603 A and are available from the assignee, Novo, as DURAMYL[®]. Other particularly preferred oxidative stability enhanced amylase include those described in WO 9418314 to Genencor International and WO 9402597 to Novo. Any other oxidative stability-enhanced amylase can be used, for example as derived by site-directed mutagenesis from known chimeric, hybrid or simple mutant parent forms of available amylases. Other preferred enzyme modifications are accessible. See WO 9509909 A to Novo.

Bleach Catalysts - The present invention compositions and methods utilize metal-containing bleach catalysts that are effective for use in ADD compositions. Preferred are manganese and cobalt-containing bleach catalysts.

One type of metal-containing bleach catalyst is a catalyst system comprising a transition metal cation of defined bleach catalytic activity, such as copper, iron, titanium, ruthenium tungsten, molybdenum, or manganese cations, an auxiliary metal cation having little or no bleach catalytic activity, such as zinc or aluminum cations, and a sequester having defined stability constants for the catalytic and auxiliary metal cations, particularly ethylenediaminetetraacetic acid, ethylenediaminetetra (methylenephosphonic acid) and water-soluble salts thereof. Such catalysts are disclosed in U.S. Pat. 4,430,243.

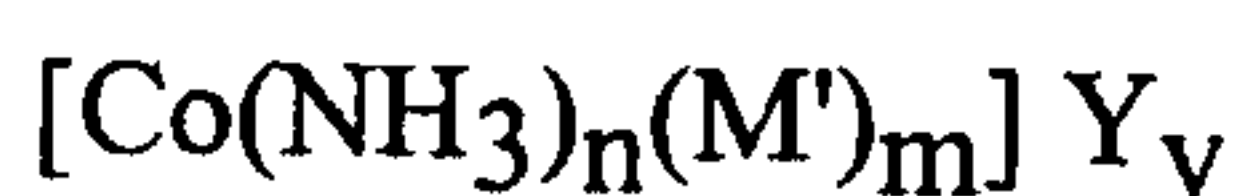
Other types of bleach catalysts include the manganese-based complexes disclosed in U.S. Pat. 5,246,621 and U.S. Pat. 5,244,594. Preferred examples of these catalysts include $\text{Mn}^{\text{IV}}_2(\text{u-O})_3(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2(\text{PF}_6)_2$ ("MnTACN"), $\text{Mn}^{\text{III}}_2(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2(\text{ClO}_4)_2$, $\text{Mn}^{\text{IV}}_4(\text{u-O})_6(1,4,7\text{-triazacyclononane})_4(\text{ClO}_4)_2$, $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}_4(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2(\text{ClO}_4)_3$, and mixtures thereof. See also European patent application publication no. 549,272. Other ligands suitable for use herein include 1,5,9-trimethyl-1,5,9-triazacyclododecane, 2-methyl-1,4,7-triazacyclononane, 2-methyl-1,4,7-triazacyclononane, and mixtures thereof.

The bleach catalysts useful in automatic dishwashing compositions and concentrated powder detergent compositions may also be selected as appropriate for the present invention. For examples of suitable bleach catalysts see U.S. Pat. 4,246,612 and U.S. Pat. 5,227,084.

Other bleach catalysts are described, for example, in European patent application, publication no. 408,131 (cobalt complex catalysts), European patent applications, publication nos. 384,503, and 306,089 (metallo-porphyrin catalysts), U.S. 4,728,455 (manganese/multidentate ligand catalyst), U.S. 4,711,748 and European patent application, publication no. 224,952, (absorbed manganese on aluminosilicate catalyst), U.S. 4,601,845 (aluminosilicate support with manganese and zinc or magnesium salt), U.S. 4,626,373 (manganese/ligand catalyst), U.S. 4,119,557 (ferric complex catalyst),

German Pat. specification 2,054,019 (cobalt chelant catalyst) Canadian 866,191 (transition metal-containing salts), U.S. 4,430,243 (chelants with manganese cations and non-catalytic metal cations), and U.S. 4,728,455 (manganese gluconate catalysts).

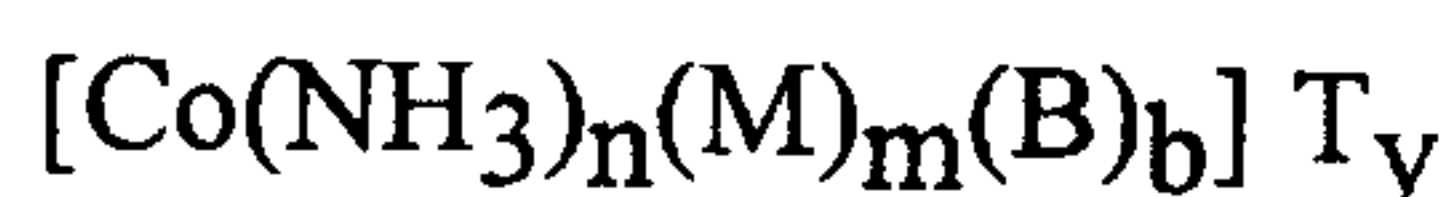
Preferred are cobalt catalysts which have the formula:



wherein n is an integer from 3 to 5 (preferably 4 or 5; most preferably 5); M' is a labile coordinating moiety, preferably selected from the group consisting of chlorine, bromine, hydroxide, water, and (when m is greater than 1) combinations thereof; m is an integer from 1 to 3 (preferably 1 or 2; most preferably 1); $m+n = 6$; and Y is an appropriately selected counteranion present in a number y, which is an integer from 1 to 3 (preferably 2 to 3; most preferably 2 when Y is a -1 charged anion), to obtain a charge-balanced salt.

The preferred cobalt catalyst of this type useful herein are cobalt pentaamine chloride salts having the formula $[\text{Co}(\text{NH}_3)_5\text{Cl}] \text{Y}_y$, and especially $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$.

More preferred are the present invention compositions which utilize cobalt (III) bleach catalysts having the formula:



wherein cobalt is in the +3 oxidation state; n is 4 or 5 (preferably 5); M is one or more ligands coordinated to the cobalt by one site; m is 0, 1 or 2 (preferably 1); B is a ligand coordinated to the cobalt by two sites; b is 0 or 1 (preferably 0), and when $b=0$, then $m+n = 6$, and when $b=1$, then $m=0$ and $n=4$; and T is one or more appropriately selected counteranions present in a number y, where y is an integer to obtain a charge-balanced salt (preferably y is 1 to 3; most preferably 2 when T is a -1 charged anion); and wherein further said catalyst has a base hydrolysis rate constant of less than $0.23 \text{ M}^{-1} \text{ s}^{-1}$ (25°C).

Preferred T are selected from the group consisting of chloride, iodide, I_3^- , formate, nitrate, nitrite, sulfate, sulfite, citrate, acetate, carbonate, bromide, PF_6^- , BF_4^- , $\text{B}(\text{Ph})_4^-$, phosphate, phosphite, silicate, tosylate, methanesulfonate, and combinations thereof. Optionally, T can be protonated if more than one anionic group exists in T, e.g., HPO_4^{2-} , HCO_3^- , H_2PO_4^- , etc. Further, T may be selected from the group consisting of

non-traditional inorganic anions such as anionic surfactants (e.g., linear alkylbenzene sulfonates (LAS), alkyl sulfates (AS), alkylethoxysulfonates (AES), etc.) and/or anionic polymers (e.g., polyacrylates, polymethacrylates, etc.).

The M moieties include, but are not limited to, for example, F^- , SO_4^{2-} , NCS^- , SCN^- , $S_2O_3^{2-}$, NH_3 , PO_4^{3-} , and carboxylates (which preferably are mono-carboxylates, but more than one carboxylate may be present in the moiety as long as the binding to the cobalt is by only one carboxylate per moiety, in which case the other carboxylate in the M moiety may be protonated or in its salt form). Optionally, M can be protonated if more than one anionic group exists in M (e.g., HPO_4^{2-} , HCO_3^- , $H_2PO_4^-$, $HOC(O)CH_2C(O)O^-$, etc.) Preferred M moieties are substituted and unsubstituted C_1 - C_{30} carboxylic acids having the formulas:



wherein R is preferably selected from the group consisting of hydrogen and C_1 - C_{30} (preferably C_1 - C_{18}) unsubstituted and substituted alkyl, C_6 - C_{30} (preferably C_6 - C_{18}) unsubstituted and substituted aryl, and C_3 - C_{30} (preferably C_5 - C_{18}) unsubstituted and substituted heteroaryl, wherein substituents are selected from the group consisting of $-NR'_3$, $-NR'_4^+$, $-C(O)OR'$, $-OR'$, $-C(O)NR'_2$, wherein R' is selected from the group consisting of hydrogen and C_1 - C_6 moieties. Such substituted R therefore include the moieties $-(CH_2)_nOH$ and $-(CH_2)_nNR'_4^+$, wherein n is an integer from 1 to about 16, preferably from about 2 to about 10, and most preferably from about 2 to about 5.

Most preferred M are carboxylic acids having the formula above wherein R is selected from the group consisting of hydrogen, methyl, ethyl, propyl, straight or branched C_4 - C_{12} alkyl, and benzyl. Most preferred R is methyl. Preferred carboxylic acid M moieties include formic, benzoic, octanoic, nonanoic, decanoic, dodecanoic, malonic, maleic, succinic, adipic, phthalic, 2-ethylhexanoic, naphthenoic, oleic, palmitic, triflate, tartrate, stearic, butyric, citric, acrylic, aspartic, fumaric, lauric, linoleic, lactic, malic, and especially acetic acid.

The B moieties include carbonate, di- and higher carboxylates (e.g., oxalate, malonate, malic, succinate, maleate), picolinic acid, and alpha and beta amino acids (e.g., glycine, alanine, beta-alanine, phenylalanine).

Cobalt bleach catalysts useful herein are known, being described for example along with their base hydrolysis rates, in M. L. Tobe, "Base Hydrolysis of Transition-Metal Complexes", Adv. Inorg. Bioinorg. Mech., (1983), 2, pages 1-94. For example, Table 1 at page 17, provides the base hydrolysis rates (designated therein as k_{OH}) for cobalt pentaamine catalysts complexed with oxalate ($k_{OH} = 2.5 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ (25°C)), NCS^- ($k_{OH} = 5.0 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ (25°C)), formate ($k_{OH} = 5.8 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ (25°C)), and acetate ($k_{OH} = 9.6 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ (25°C)). The most preferred cobalt catalyst useful herein are cobalt pentaamine acetate salts having the formula $[\text{Co}(\text{NH}_3)_5\text{OAc}] \text{ T}_y$, wherein OAc represents an acetate moiety, and especially cobalt pentaamine acetate chloride, $[\text{Co}(\text{NH}_3)_5\text{OAc}]\text{Cl}_2$; as well as $[\text{Co}(\text{NH}_3)_5\text{OAc}](\text{OAc})_2$; $[\text{Co}(\text{NH}_3)_5\text{OAc}](\text{PF}_6)_2$; $[\text{Co}(\text{NH}_3)_5\text{OAc}](\text{SO}_4)$; $[\text{Co}(\text{NH}_3)_5\text{OAc}](\text{BF}_4)_2$; and $[\text{Co}(\text{NH}_3)_5\text{OAc}](\text{NO}_3)_2$.

Cobalt catalysts according to the present invention made be produced according to the synthetic routes disclosed in U.S. Patent Nos. 5,559,261, 5,581,005, and 5,597,936.

These catalysts may be coprocessed with adjunct materials so as to reduce the color impact if desired for the aesthetics of the product, or to be included in enzyme-containing particles as exemplified hereinafter, or the compositions may be manufactured to contain catalyst "speckles".

As a practical matter, and not by way of limitation, the cleaning compositions and cleaning processes herein can be adjusted to provide on the order of at least one part per hundred million of the active bleach catalyst species in the aqueous washing medium, and will preferably provide from about 0.01 ppm to about 25 ppm, more preferably from about 0.05 ppm to about 10 ppm, and most preferably from about 0.1 ppm to about 5 ppm, of the bleach catalyst species in the wash liquor. In order to obtain such levels the compositions herein will comprise from about 0.0005% to about 0.2%, more preferably

from about 0.004% to about 0.08%, of bleach catalyst by weight of the cleaning compositions.

Preferred bleach catalysts, along with methods of their use can be additionally found in U.S. Patents 5,705,464, 5,804,542, 5,798,326, 5,703,030 and 5,599,781.

Conventional Cleaning agents

These conventional cleaning agents are preferably present in the cleaning compositions of the present invention. Suitable conventional cleaning agents include builders, surfactants, enzymes other than amylase, bleach activators, bleach boosters, bleaches, alkalinity sources, colorants, perfume, lime soap dispersants, polymeric dye transfer inhibiting agents, antibacterial agent, crystal growth inhibitors, photobleaches, heavy metal ion sequestrants, anti-tarnishing agents, anti-microbial agents, anti-oxidants, anti-redeposition agents, soil release polymers, electrolytes, pH modifiers, thickeners, abrasives, divalent metal ions, metal ion salts, enzyme stabilizers, corrosion inhibitors, diamines, suds stabilizing polymers, solvents, process aids, fabric softening agents, optical brighteners, hydrotropes, and mixtures thereof.

Detergent Builders

The present invention may include an optional builder in the product composition. The level of detergent salt/builder can vary widely depending upon the end use of the composition and its desired physical form. When present, the compositions will typically comprise at least about 1% detergent builder and more typically from about 10% to about 80%, even more typically from about 15% to about 50% by weight, of the detergent builder. Lower or higher levels, however, are not meant to be excluded.

Inorganic or P-containing detergent builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the tripolyphosphates, pyrophosphates, and glassy polymeric meta-phosphates), phosphonates, phytic acid, silicates, carbonates (including bicarbonates and sesquicarbonates), sulphates, and aluminosilicates. However, non-phosphate salts are required in some locales. Importantly, the compositions herein function surprisingly well even in the presence of the so-called "weak" builders (as compared with phosphates)

such as citrate, or in the so-called "underbuilt" situation that may occur with zeolite or layered silicate builders.

Examples of silicate builders are the alkali metal silicates, particularly those having a $\text{SiO}_2:\text{Na}_2\text{O}$ ratio in the range 1.6:1 to 3.2:1 and layered silicates, such as the layered sodium silicates described in U.S. Patent 4,664,839, issued May 12, 1987 to H. P. Rieck. NaSKS-6 is the trademark for a crystalline layered silicate marketed by Hoechst (commonly abbreviated herein as "SKS-6"). Unlike zeolite builders, the Na SKS-6 silicate builder does not contain aluminum. NaSKS-6 has the delta- Na_2SiO_3 morphology form of layered silicate. It can be prepared by methods such as those described in German DE-A-3,417,649 and DE-A-3,742,043. SKS-6 is a highly preferred layered silicate for use herein, but other such layered silicates, such as those having the general formula $\text{NaMSixO}_{2x+1}\cdot y\text{H}_2\text{O}$ wherein M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2, and y is a number from 0 to 20, preferably 0 can be used herein. Various other layered silicates from Hoechst include NaSKS-5TM, NaSKS-7TM and NaSKS-11TM, as the alpha, beta and gamma forms. As noted above, the delta- Na_2SiO_3 (NaSKS-6 form) is most preferred for use herein. Other silicates may also be useful such as for example magnesium silicate, which can serve as a crispening agent in granular formulations, as a stabilizing agent for oxygen bleaches, and as a component of suds control systems.

Examples of carbonate salts as builders are the alkaline earth and alkali metal carbonates as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973.

Aluminosilicate builders may also be added to the present invention as a detergent salt. Aluminosilicate builders are of great importance in most currently marketed heavy duty granular detergent compositions. Aluminosilicate builders include those having the empirical formula:



wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to about 0.5, and x is an integer from about 15 to about 264.

Useful aluminosilicate ion exchange materials are commercially available. These aluminosilicates can be crystalline or amorphous in structure and can be naturally-

occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. Patent 3,985,669, Krummel, et al, issued October 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite P (B), Zeolite MAP and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula:



wherein x is from about 20 to about 30, especially about 27. This material is known as Zeolite A. Dehydrated zeolites ($x = 0 - 10$) may also be used herein. Preferably, the aluminosilicate has a particle size of about 0.1-10 microns in diameter.

Organic detergent builders suitable for the purposes of the present invention include, but are not restricted to, a wide variety of polycarboxylate compounds. As used herein, "polycarboxylate" refers to compounds having a plurality of carboxylate groups, preferably at least 3 carboxylates. Polycarboxylate builder can generally be added to the composition in acid form, but can also be added in the form of a neutralized salt. When utilized in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred.

Included among the polycarboxylate builders are a variety of categories of useful materials. One important category of polycarboxylate builders encompasses the ether polycarboxylates, including oxydisuccinate, as disclosed in Berg, U.S. Patent 3,128,287, issued April 7, 1964, and Lamberti et al, U.S. Patent 3,635,830, issued January 18, 1972. See also "TMS/TDS" builders of U.S. Patent 4,663,071, issued to Bush et al, on May 5, 1987. Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. Patents 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903.

Other useful detergency builders include the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid, and carboxymethyloxysuccinic acid, the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates such

as mellitic acid, succinic acid, oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are polycarboxylate builders of particular importance. Oxydisuccinates are also especially useful in such compositions and combinations.

Also suitable in the detergent compositions of the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. Patent 4,566,984, Bush, issued January 28, 1986. Useful succinic acid builders include the C5-C20 alkyl and alkenyl succinic acids and salts thereof. A particularly preferred compound of this type is dodecenylsuccinic acid. Specific examples of succinate builders include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Laurylsuccinates are the preferred builders of this group, and are described in European Patent Application 86200690.5/0,200,263, published November 5, 1986.

Other suitable polycarboxylates are disclosed in U.S. Patent 4,144,226, Crutchfield et al, issued March 13, 1979 and in U.S. Patent 3,308,067, Diehl, issued March 7, 1967. See also Diehl U.S. Patent 3,723,322.

Fatty acids, e.g., C12-C18 monocarboxylic acids, can also be incorporated into the compositions alone, or in combination with the aforesaid builders, especially citrate and/or the succinate builders, to provide additional builder activity. Such use of fatty acids will generally result in a diminution of sudsing, which should be taken into account by the formulator.

Surfactants

Surfactants may be included in the compositions of the present invention as ultrasonic cleaning agent. The surfactant may comprise from about 0.01%, to about 99.9%, by weight of the composition depending upon the particular surfactants used and the effects desired. More typical levels comprise from about 0.1% to about 80%, even more preferably from about 0.5% to about 60%, by weight of the composition. Examples of suitable surfactants can be found in McCutcheon's EMULSIFIERS AND DETERGENTS, North American Edition, 1997, McCutcheon Division, MC Publishing Company, in U.S. 3,929,678, Dec. 30, 1975 Laughlin, et al, and U.S. 4,259,217, March

31, 1981, Murphy; in the series "Surfactant Science", Marcel Dekker, Inc., New York and Basel; in "Handbook of Surfactants", M.R. Porter, Chapman and Hall, 2nd Ed., 1994; in "Surfactants in Consumer Products", Ed. J. Falbe, Springer-Verlag, 1987 and "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch).

The deterative surfactant can be nonionic, anionic, ampholytic, zwitterionic, or cationic. Mixtures of these surfactants can also be used. Preferred detergent compositions comprise anionic deterative surfactants or mixtures of anionic surfactants with other surfactants, especially nonionic surfactants and/or amphoteric surfactants.

Nonlimiting examples of surfactants useful herein include the conventional C11-C18 alkyl benzene sulfonates and primary, secondary and random alkyl sulfates, the C10-C18 alkyl alkoxy sulfates, the C10-C18 alkyl polyglycosides and their corresponding sulfated polyglycosides, C12-C18 alpha-sulfonated fatty acid esters, C12-C18 alkyl and alkyl phenol alkoxylates (especially ethoxylates and mixed ethoxy/propoxy), C12-C18 betaines and sulfobetaines ("sultaines"), C10-C18 amine oxides, C₆ to C₁₈ branched or linear alkyl sulfates, C₆ to C₁₈ branched or linear alkyl benzene sulfonates, C₆ to C₁₈ branched or linear alkyl alkoxy sulfates, and mixtures thereof. and the like. Other conventional useful surfactants are listed in standard texts.

Anionic Surfactants -

The anionic surfactants useful in the present invention are preferably selected from the group consisting of, linear alkylbenzene sulfonate, alpha olefin sulfonate, paraffin sulfonates, alkyl ester sulfonates, alkyl sulfates, alkyl alkoxy sulfate, alkyl sulfonates, alkyl alkoxy carboxylate, alkyl alkoxylated sulfates, sarcosinates, taurinates, and mixtures thereof, more preferably C₆ to C₁₈ branched or linear alkyl sulfates, C₆ to C₁₈ branched or linear alkyl benzene sulfonates, C₆ to C₁₈ branched or linear alkyl alkoxy sulfates, and mixtures thereof. An effective amount, typically from about 0.5% to about 90%, preferably about 5% to about 60%, more preferably from about 10 to about 30%, by weight of anionic deterative surfactant can be used in the present invention.

Alkyl sulfate surfactants are another type of anionic surfactant of importance for use herein. In addition to providing excellent overall cleaning ability when used in combination with polyhydroxy fatty acid amides (see below), including good grease/oil

cleaning over a wide range of temperatures, wash concentrations, and wash times, dissolution of alkyl sulfates can be obtained, as well as improved formulability in liquid detergent formulations are water soluble salts or acids of the formula ROSO_3M wherein R preferably is a $\text{C}_{10}\text{-C}_{24}$ hydrocarbyl, preferably an alkyl or hydroxyalkyl having a $\text{C}_{10}\text{-C}_{20}$ alkyl component, more preferably a $\text{C}_{12}\text{-C}_{18}$ alkyl or hydroxyalkyl, and M is H or a cation, e.g., an alkali (Group IA) metal cation (e.g., sodium, potassium, lithium), substituted or unsubstituted ammonium cations such as methyl-, dimethyl-, and trimethyl ammonium and quaternary ammonium cations, e.g., tetramethyl-ammonium and dimethyl piperdinium, and cations derived from alkanolamines such as ethanolamine, diethanolamine, triethanolamine, and mixtures thereof, and the like. Typically, alkyl chains of $\text{C}_{12}\text{-C}_{16}$ are preferred for lower wash temperatures (e.g., below about 50°C) and $\text{C}_{16}\text{-C}_{18}$ alkyl chains are preferred for higher wash temperatures (e.g., above about 50°C).

Alkyl alkoxyated sulfate surfactants are another category of useful anionic surfactant. These surfactants are water soluble salts or acids typically of the formula $\text{RO(A)}_m\text{SO}_3\text{M}$ wherein R is an unsubstituted $\text{C}_{10}\text{-C}_{24}$ alkyl or hydroxyalkyl group having a $\text{C}_{10}\text{-C}_{24}$ alkyl component, preferably a $\text{C}_{12}\text{-C}_{20}$ alkyl or hydroxyalkyl, more preferably $\text{C}_{12}\text{-C}_{18}$ alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, m is greater than zero, typically between about 0.5 and about 6, more preferably between about 0.5 and about 3, and M is H or a cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, etc.), ammonium or substituted-ammonium cation. Alkyl ethoxylated sulfates as well as alkyl propoxylated sulfates are contemplated herein. Specific examples of substituted ammonium cations include methyl-, dimethyl-, trimethyl-ammonium and quaternary ammonium cations, such as tetramethyl-ammonium, dimethyl piperidinium and cations derived from alkanolamines, e.g. monoethanolamine, diethanolamine, and triethanolamine, and mixtures thereof. Exemplary surfactants are $\text{C}_{12}\text{-C}_{18}$ alkyl polyethoxylate (1.0) sulfate, $\text{C}_{12}\text{-C}_{18}$ alkyl polyethoxylate (2.25) sulfate, $\text{C}_{12}\text{-C}_{18}$ alkyl polyethoxylate (3.0) sulfate, and $\text{C}_{12}\text{-C}_{18}$ alkyl polyethoxylate (4.0) sulfate wherein M is conveniently selected from sodium and potassium. Surfactants for use herein can be made from natural or synthetic alcohol

feedstocks. Chain lengths represent average hydrocarbon distributions, including branching.

Examples of suitable anionic surfactants are given in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A variety of such surfactants are also generally disclosed in U.S. Patent 3,929,678, issued December 30, 1975 to Laughlin, et al. at Column 23, line 58 through Column 29, line 23.

Another possible surfactant are the so-called Dianionics. These are surfactants which have at least two anionic groups present on the surfactant molecule. Some suitable dianionic surfactants are further described in WO98/00498; US 5,958,858; WO98/05742 and WO98/05749.

Other conventional useful surfactants are listed in standard texts.

Nonionic Surfactants - One particularly preferred surfactants are nonionic surfactants. Nonionic surfactants may be present in amounts from 0.01% to about 40% by weight, preferably from about 0.1% to about 30%, and most preferably from about 0.25% to about 20%.

Particularly preferred in the present invention include mixed nonionic surfactants. While a wide range of nonionic surfactants may be selected from for purposes of the mixed nonionic surfactant systems useful in the present invention compositions, it is preferred that the nonionic surfactants comprise both a low cloud point surfactant as represented by the ether capped poly(oxyalkylated) alcohol surfactant and high cloud point nonionic surfactant(s) as described as follows. "Cloud point", as used herein, is a well known property of nonionic surfactants which is the result of the surfactant becoming less soluble with increasing temperature, the temperature at which the appearance of a second phase is observable is referred to as the "cloud point" (See Kirk Othmer, pp. 360-362, *ibid*).

As used herein, a "low cloud point" nonionic surfactant is defined as a nonionic surfactant system ingredient having a cloud point of less than 30°C, preferably less than

about 20°C, and most preferably less than about 10°C and is represented by the ether-capped poly(oxyalkylated) alcohols as described herein.

Of course, other low-cloud point surfactants may be included in conjunction with the ether-capped poly(oxyalkylated) surfactants. Such optional low-cloud point surfactants include nonionic alkoxylated surfactants, especially ethoxylates derived from primary alcohol, and polyoxypropylene/polyoxyethylene/polyoxypropylene (PO/EO/PO) reverse block polymers. Also, such low cloud point nonionic surfactants include, for example, ethoxylated-propoxylated alcohol (e.g., Olin Corporation's Poly-Tergent® SLF18) and epoxy-capped poly(oxyalkylated) alcohols (e.g., Olin Corporation's Poly-Tergent® SLF18B series of nonionics, as described, for example, in WO 94/22800, published October 13, 1994 by Olin Corporation). These nonionic surfactants can optionally contain propylene oxide in an amount up to about 15% by weight. Other preferred nonionic surfactants can be prepared by the processes described in U.S. Patent 4,223,163, issued September 16, 1980, Builloty.

Optional low cloud point nonionic surfactants additionally comprise a polyoxyethylene, polyoxypropylene block polymeric compound. Block polyoxyethylene-polyoxypropylene polymeric compounds include those based on ethylene glycol, propylene glycol, glycerol, trimethylolpropane and ethylenediamine as initiator reactive hydrogen compound. Certain of the block polymer surfactant compounds designated PLURONIC®, REVERSED PLURONIC®, and TETRONIC® by the BASF-Wyandotte Corp., Wyandotte, Michigan, are suitable in ADD compositions of the invention. Preferred examples include REVERSED PLURONIC® 25R2 and TETRONIC® 702. Such surfactants are typically useful herein as low cloud point nonionic surfactants.

As used herein, a "high cloud point" nonionic surfactant is defined as a nonionic surfactant system ingredient having a cloud point of greater than 40°C, preferably greater than about 50°C, and more preferably greater than about 60°C. Preferably the nonionic surfactant system comprises an ethoxylated surfactant derived from the reaction of a monohydroxy alcohol or alkylphenol containing from about 8 to about 20 carbon atoms, with from about 6 to about 15 moles of ethylene oxide per mole of alcohol or alkyl phenol on an average basis. Such high cloud point nonionic surfactants include, for

example, Tergitol™ 15S9 (supplied by Union Carbide), Rhodasurf™ TMD 8.5 (supplied by Rhone Poulenc), and Neodol™ 91-8 (supplied by Shell).

It is also preferred for purposes of the present invention that the high cloud point nonionic surfactant further have a hydrophile-lipophile balance ("HLB"; see Kirk Othmer hereinbefore) value within the range of from about 9 to about 15, preferably 11 to 15. Such materials include, for example, Tergitol 15S9 (supplied by Union Carbide), Rhodasurf TMD 8.5 (supplied by Rhone Poulenc), and Neodol 91-8 (supplied by Shell).

Another preferred high cloud point nonionic surfactant is derived from a straight or preferably branched chain or secondary fatty alcohol containing from about 6 to about 20 carbon atoms (C6-C20 alcohol), including secondary alcohols and branched chain primary alcohols. Preferably, high cloud point nonionic surfactants are branched or secondary alcohol ethoxylates, more preferably mixed C9/11 or C11/15 branched alcohol ethoxylates, condensed with an average of from about 6 to about 15 moles, preferably from about 6 to about 12 moles, and most preferably from about 6 to about 9 moles of ethylene oxide per mole of alcohol. Preferably the ethoxylated nonionic surfactant so derived has a narrow ethoxylate distribution relative to the average.

The preferred nonionic surfactant systems useful herein are mixed high cloud point and low cloud point nonionic surfactants combined in a weight ratio preferably within the range of from about 10:1 to about 1:10.

Another preferred LFNIs are the endcapped alkyl alkoxylate surfactants. Suitable endcapped alkyl alkoxylate surfactant are the epoxy-capped poly(oxyalkylated) alcohols represented by the formula:

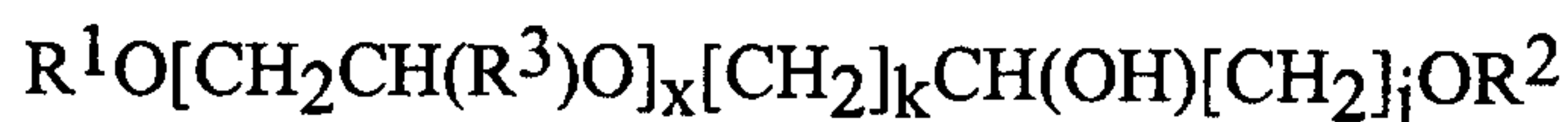


wherein R_1 is a linear or branched, aliphatic hydrocarbon radical having from 4 to 18 carbon atoms; R_2 is a linear or branched aliphatic hydrocarbon radical having from 2 to 26 carbon atoms; x is an integer having an average value of from 0.5 to 1.5, more preferably 1; and y is an integer having a value of at least 15, more preferably at least 20.

Preferably, the surfactant of formula I, at least 10 carbon atoms in the terminal epoxide unit $[CH_2CH(OH)R_2]$. Suitable surfactants of formula I, according to the

present invention, are Olin Corporation's POLY-TERGENT® SLF-18B nonionic surfactants, as described, for example, in WO 94/22800, published October 13, 1994 by Olin Corporation.

One preferred ether-capped poly(oxyalkylated) alcohols has the formula:



wherein R^1 and R^2 are linear or branched, saturated or unsaturated, aliphatic or aromatic hydrocarbon radicals having from 1 to 30 carbon atoms; R^3 is H, or a linear aliphatic hydrocarbon radical having from 1 to 4 carbon atoms; x is an integer having an average value from 1 to 30, wherein when x is 2 or greater R^3 may be the same or different and k and j are integers having an average value of from 1 to 12, and more preferably 1 to 5.

R^1 and R^2 are preferably linear or branched, saturated or unsaturated, aliphatic or aromatic hydrocarbon radicals having from 6 to 22 carbon atoms with 8 to 18 carbon atoms being most preferred. H or a linear aliphatic hydrocarbon radical having from 1 to 2 carbon atoms is most preferred for R^3 . Preferably, x is an integer having an average value of from 1 to 20, more preferably from 6 to 15.

As described above, when, in the preferred embodiments, and x is greater than 2, R^3 may be the same or different. That is, R^3 may vary between any of the alkyleneoxy units as described above. For instance, if x is 3, R^3 may be selected to form ethyleneoxy(EO) or propyleneoxy(PO) and may vary in order of (EO)(PO)(EO), (EO)(EO)(PO); (EO)(EO)(EO); (PO)(EO)(PO); (PO)(PO)(EO) and (PO)(PO)(PO). Of course, the integer three is chosen for example only and the variation may be much larger with a higher integer value for x and include, for example, multiple (EO) units and a much small number of (PO) units.

Particularly preferred surfactants as described above include those that have a low cloud point of less than 20°C. These low cloud point surfactants may then be employed in conjunction with a high cloud point surfactant as described in detail below for superior grease cleaning benefits.

Most preferred ether-capped poly(oxyalkylated) alcohol surfactants are those wherein k is 1 and j is 1 so that the surfactants have the formula:

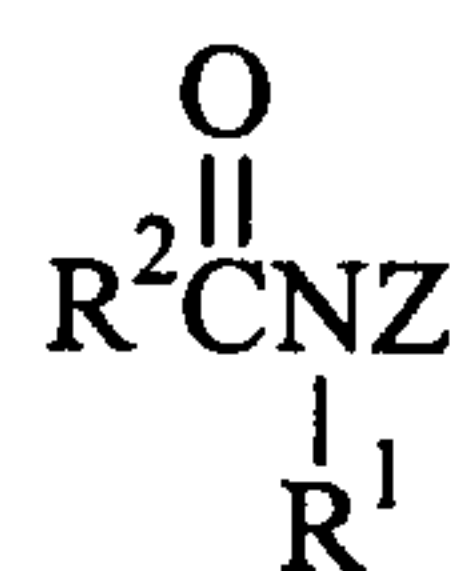


where R^1 , R^2 and R^3 are defined as above and x is an integer with an average value of from 1 to 30, preferably from 1 to 20, and even more preferably from 6 to 18. Most preferred are surfactants wherein R^1 and R^2 range from 9 to 14, R^3 is H forming ethyleneoxy and x ranges from 6 to 15.

The ether-capped poly(oxyalkylated) alcohol surfactants comprise three general components, namely a linear or branched alcohol, an alkylene oxide and an alkyl ether end cap. The alkyl ether end cap and the alcohol serve as a hydrophobic, oil-soluble portion of the molecule while the alkylene oxide group forms the hydrophilic, water-soluble portion of the molecule.

These surfactants exhibit significant improvements in spotting and filming characteristics and removal of greasy soils, when used in conjunction with high cloud point surfactants, relative to conventional surfactants.

Another suitable class of nonionic surfactants comprises sugar derived surfactants such as the polyhydroxy fatty acid amides of the formula:



wherein: R^1 is H, C_1 - C_4 hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl, or a mixture thereof, preferably C_1 - C_4 alkyl, more preferably C_1 or C_2 alkyl, most preferably C_1 alkyl (i.e., methyl); and R^2 is a C_5 - C_{31} hydrocarbyl, preferably straight chain C_7 - C_{19} alkyl or alkenyl, more preferably straight chain C_9 - C_{17} alkyl or alkenyl, most preferably straight chain C_{11} - C_{15} alkyl or alkenyl, or mixtures thereof; and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxyated derivative (preferably ethoxylated or propoxylated) thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z will be a glycityl. Suitable reducing sugars include glucose, fructose, maltose, lactose, galactose, mannose, and xylose. As raw materials, high dextrose corn syrup, high fructose corn syrup, and high maltose corn syrup can be utilized as well as the individual sugars listed above. These corn syrups

may yield a mix of sugar components for Z. It should be understood that it is by no means intended to exclude other suitable raw materials. Z preferably will be selected from the group consisting of $-\text{CH}_2-(\text{CHOH})_n-\text{CH}_2\text{OH}$, $-\text{CH}(\text{CH}_2\text{OH})-(\text{CHOH})_{n-1}-\text{CH}_2\text{OH}$, $-\text{CH}_2-(\text{CHOH})_2(\text{CHOR}')(\text{CHOH})-\text{CH}_2\text{OH}$, and alkoxylated derivatives thereof, where n is an integer from 3 to 5, inclusive, and R' is H or a cyclic or aliphatic monosaccharide. Most preferred are glycityls wherein n is 4, particularly $-\text{CH}_2-(\text{CHOH})_4-\text{CH}_2\text{OH}$.

R' can be, for example, N-methyl, N-ethyl, N-propyl, N-isopropyl, N-butyl, N-2-hydroxy ethyl, or N-2-hydroxy propyl.

$\text{R}^2-\text{CO}-\text{N}<$ can be, for example, cocamide, stearamide, oleamide, lauramide, myristamide, capricamide, palmitamide, tallowamide, etc.

Z can be 1-deoxyglucityl, 2-deoxyfructityl, 1-deoxymaltityl, 1-deoxylactityl, 1-deoxygalactityl, 1-deoxymannityl, 1-deoxymaltotriosityl, etc.

Methods for making polyhydroxy fatty acid amides are known in the art. In general, they can be made by reacting an alkyl amine with a reducing sugar in a reductive amination reaction to form a corresponding N-alkyl polyhydroxyamine, and then reacting the N-alkyl polyhydroxyamine with a fatty aliphatic ester or triglyceride in a condensation/amidation step to form the N-alkyl, N-polyhydroxy fatty acid amide product. Processes for making compositions containing polyhydroxy fatty acid amides are disclosed, for example, in G.B. Patent Specification 809,060, published February 18, 1959, by Thomas Hedley & Co., Ltd., U.S. Patent 2,965,576, issued December 20, 1960 to E. R. Wilson, and U.S. Patent 2,703,798, Anthony M. Schwartz, issued March 8, 1955, and U.S. Patent 1,985,424, issued December 25, 1934 to Piggott.

The preferred alkylpolyglycosides have the formula



wherein R^2 is selected from the group consisting of alkyl, alkyl-phenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from about 10 to about 18, preferably from about 12 to about 14, carbon atoms; n is 2 or 3, preferably 2; t is from 0 to about 10, preferably 0; and x is from about 1.3 to about 10,

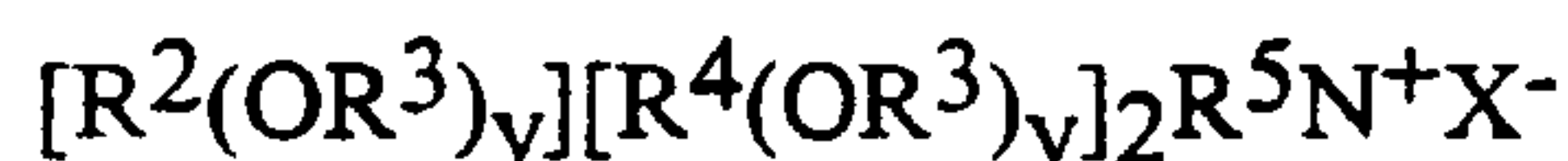
preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7. The glycosyl is preferably derived from glucose. To prepare these compounds, the alcohol or alkylpolyethoxy alcohol is formed first and then reacted with glucose, or a source of glucose, to form the glucoside (attachment at the 1-position). The additional glycosyl units can then be attached between their 1-position and the preceding glycosyl units 2-, 3-, 4- and/or 6-position, preferably predominantly the 2-position.

These and other nonionic surfactants are well known in the art, being described in more detail in Kirk Othmer's Encyclopedia of Chemical Technology, 3rd Ed., Vol. 22, pp. 360-379, "Surfactants and Detersive Systems".

Further suitable nonionic detergent surfactants are generally disclosed in U.S. Patent 3,929,678, Laughlin et al., issued December 30, 1975, at column 13, line 14 through column 16, line 6.

Cationic Surfactants -

Cationic surfactants suitable for use in the compositions of the present invention include those having a long-chain hydrocarbyl group. Examples of such cationic co-surfactants include the ammonium co-surfactants such as alkyl dimethylammonium halogenides, and those co-surfactants having the formula:

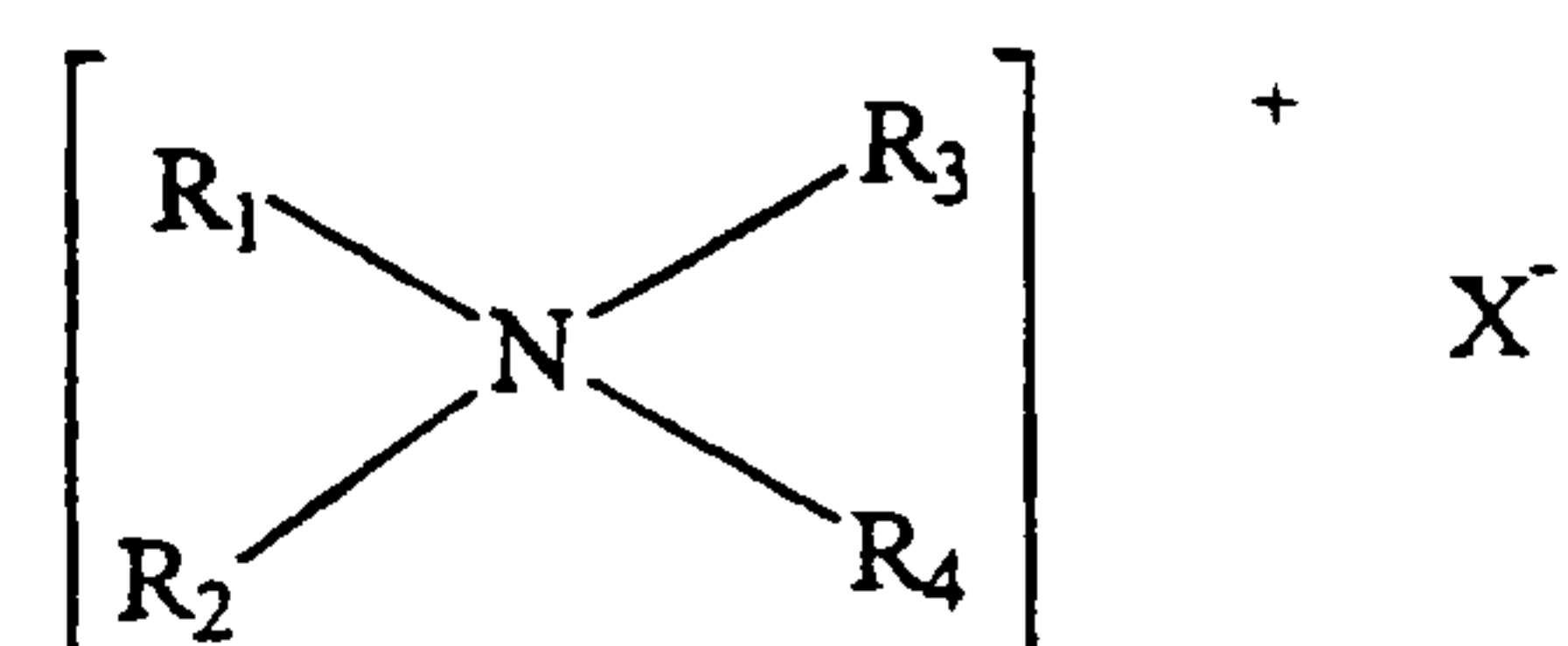


wherein R^2 is an alkyl or alkyl benzyl group having from 8 to 18 carbon atoms in the alkyl chain, each R^3 is selected from the group consisting of $-CH_2CH_2-$, $-CH_2CH(CH_3)-$, $-CH_2CH(CH_2OH)-$, $-CH_2CH_2CH_2-$, and mixtures thereof; each R^4 is selected from the group consisting of C_1 - C_4 alkyl, C_1 - C_4 hydroxyalkyl, benzyl ring structures formed by joining the two R^4 groups, $-CH_2CHOH-CHOHCOR^6CHOHCH_2OH$ wherein R^6 is any hexose or hexose polymer having a molecular weight less than about 1000, and hydrogen when y is not 0; R^5 is the same as R^4 or is an alkyl chain wherein the total number of carbon atoms of R^2 plus R^5 is not more than about 18; each y is from 0 to about 10 and the sum of the y values is from 0 to about 15; and X is any compatible anion.

Examples of other suitable cationic surfactants are described in following documents:

M.C. Publishing Co., McCutcheon's, Detergents & Emulsifiers, (North American edition 1997); Schwartz, et al., Surface Active Agents, Their Chemistry and Technology, New York: Interscience Publishers, 1949; U.S. Patent 3,155,591; U. S. Patent 3,929,678; U. S. Patent 3,959,461 U. S. Patent 4,387,090 and U.S. Patent 4,228,044.

Examples of suitable cationic surfactants are those corresponding to the general formula:



wherein R_1 , R_2 , R_3 , and R_4 are independently selected from an aliphatic group of from 1 to about 22 carbon atoms or an aromatic, alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, aryl or alkylaryl group having up to about 22 carbon atoms; and X is a salt-forming anion such as those selected from halogen, (e.g. chloride, bromide), acetate, citrate, lactate, glycolate, phosphate nitrate, sulfate, and alkylsulfate radicals. The aliphatic groups can contain, in addition to carbon and hydrogen atoms, ether linkages, and other groups such as amino groups. The longer chain aliphatic groups, e.g., those of about 12 carbons, or higher, can be saturated or unsaturated. Preferred is when R_1 , R_2 , R_3 , and R_4 are independently selected from C1 to about C22 alkyl. Especially preferred are cationic materials containing two long alkyl chains and two short alkyl chains or those containing one long alkyl chain and three short alkyl chains. The long alkyl chains in the compounds described in the previous sentence have from about 12 to about 22 carbon atoms, preferably from about 16 to about 22 carbon atoms, and the short alkyl chains in the compounds described in the previous sentence have from 1 to about 3 carbon atoms, preferably from 1 to about 2 carbon atoms.

Suitable levels of cationic deterative surfactant herein, when present, are from about 0.1% to about 20%, preferably from about 1% to about 15%, although much higher levels, e.g., up to about 30% or more, may be useful especially in nonionic : cationic (i.e., limited or anionic-free) formulations.

Other Surfactants -

Amphoteric or zwitterionic deterative surfactants when present are usually useful at levels in the range from about 0.1% to about 20% by weight of the detergent composition. Often levels will be limited to about 5% or less, especially when the amphoteric is costly.

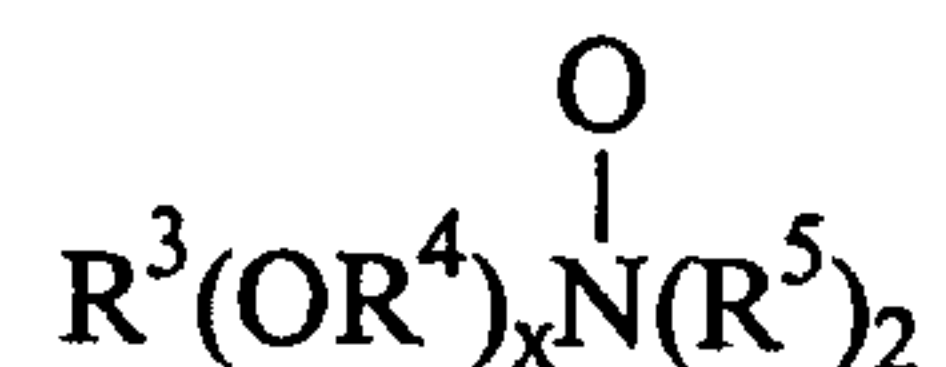
Suitable amphoteric surfactants include the amine oxides corresponding to the formula:



wherein R is a primary alkyl group containing 6-24 carbons, preferably 10-18 carbons, and wherein R' and R'' are, each, independently, an alkyl group containing 1 to 6 carbon atoms. The arrow in the formula is a conventional representation of a semi-polar bond.

Amine oxides are semi-polar surfactants and include water-soluble amine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to about 3 carbon atoms.

Preferred amine oxide surfactants having the formula

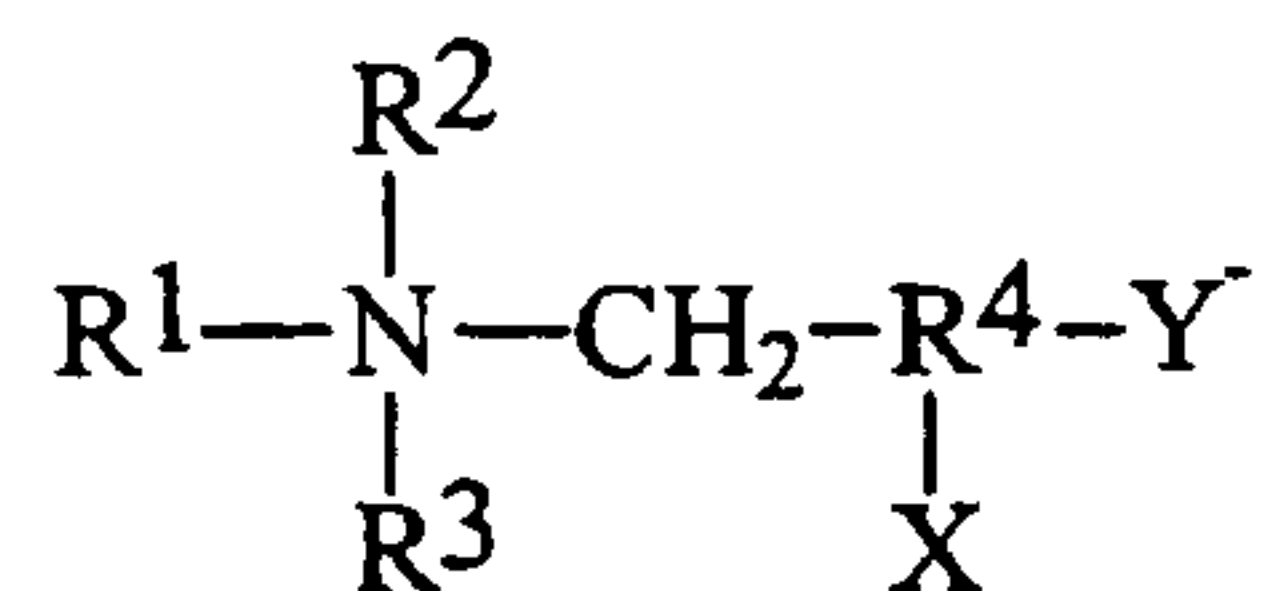


wherein R³ is an alkyl, hydroxyalkyl, or alkyl phenyl group or mixtures thereof containing from about 8 to about 22 carbon atoms; R⁴ is an alkylene or hydroxyalkylene group containing from about 2 to about 3 carbon atoms or mixtures thereof; x is from 0 to about 3; and each R⁵ is an alkyl or hydroxyalkyl group containing from about 1 to about 3 carbon atoms or a polyethylene oxide group containing from about 1 to about 3 ethylene oxide groups. The R⁵ groups can be attached to each other, e.g., through an oxygen or nitrogen atom, to form a ring structure.

These amine oxide surfactants in particular include C₁₀-C₁₈ alkyl dimethyl amine oxides and C₈-C₁₂ alkoxy ethyl dihydroxy ethyl amine oxides. Preferably the amine oxide is present in the composition in an effective amount, more preferably from about 0.1% to about 20%, even more preferably about 0.1% to about 15%, even more preferably still from about 0.5% to about 10%, by weight.

Some suitable zwitterionic surfactants which can be used herein comprise the betaine and betaine-like surfactants wherein the molecule contains both basic and acidic groups which form an inner salt giving the molecule both cationic and anionic hydrophilic groups over a broad range of pH values. Some common examples of these are described in U.S. Pat. Nos. 2,082,275, 2,702,279 and 2,255,082.

One of the preferred zwitterionic compounds have the formula



wherein R¹ is an alkyl radical containing from 8 to 22 carbon atoms, R² and R³ contain from 1 to 3 carbon atoms, R⁴ is an alkylene chain containing from 1 to 3 carbon atoms, X is selected from the group consisting of hydrogen and a hydroxyl radical, Y is selected from the group consisting of carboxyl and sulfonyl radicals and wherein the sum of R¹, R² and R³ radicals is from 14 to 24 carbon atoms.

Zwitterionic surfactants, as mentioned hereinbefore, contain both a cationic group and an anionic group and are in substantial electrical neutrality where the number of anionic charges and cationic charges on the surfactant molecule are substantially the same. Zwitterionics, which typically contain both a quaternary ammonium group and an anionic group selected from sulfonate and carboxylate groups are desirable since they maintain their amphoteric character over most of the pH range of interest for cleaning hard surfaces. The sulfonate group is the preferred anionic group.

Antimicrobial agents - an antimicrobial agent is a compound or substance that kills microorganisms or prevents or inhibits their growth and reproduction. A properly selected antimicrobial agent maintains stability under use and storage conditions (pH, temperature, light, etc.), for a required length of time. A desirable property of the

antimicrobial agent is that it is safe and nontoxic in handling, formulation and use, is environmentally acceptable and cost effective. Classes of antimicrobial agents include, but are not limited to, chlorophenols, aldehydes, biguanides, antibiotics and biologically active salts. Some preferable antimicrobial agent in the antimicrobial is bronopol, chlorhexidine diacetate, TRICOSAN™, hexetidine or parachlorometaxyleneol (PCMX). More preferably, the antimicrobial agent is TRICOSAN™, chlorhexidine diacetate or hexetidine.

The antimicrobial agent, when used, is present in a microbiocidally effective amount, more preferably from about 0.01% to about 10.0%, more preferably from about 0.1% to about 8.0%, even more preferably from about 0.5% to about 2.0%, by weight of the composition.

Bleaching Agents

Hydrogen peroxide sources are described in detail in the herein incorporated Kirk Othmer's Encyclopedia of Chemical Technology, 4th Ed (1992, John Wiley & Sons), Vol. 4, pp. 271-300 "Bleaching Agents (Survey)", and include the various forms of sodium perborate and sodium percarbonate, including various coated and modified forms. An "effective amount" of a source of hydrogen peroxide is any amount capable of measurably improving stain removal (especially of tea stains) from soiled dishware compared to a hydrogen peroxide source-free composition when the soiled dishware is washed by the consumer in a domestic automatic dishwasher in the presence of alkali.

More generally a source of hydrogen peroxide herein is any convenient compound or mixture which under consumer use conditions provides an effective amount of hydrogen peroxide. Levels may vary widely and are usually in the range from about 0.1% to about 70%, more typically from about 0.5% to about 30%, by weight of the compositions herein.

The preferred source of hydrogen peroxide used herein can be any convenient source, including hydrogen peroxide itself. For example, perborate, e.g., sodium perborate (any hydrate but preferably the mono- or tetra-hydrate), sodium carbonate peroxyhydrate or equivalent percarbonate salts, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, or sodium peroxide can be used herein. Also useful are sources of available oxygen such as persulfate bleach (e.g., OXONE™, manufactured by DuPont).

Sodium perborate monohydrate and sodium percarbonate are particularly preferred. Mixtures of any convenient hydrogen peroxide sources can also be used.

A preferred percarbonate bleach comprises dry particles having an average particle size in the range from about 500 micrometers to about 1,000 micrometers, not more than about 10% by weight of said particles being smaller than about 200 micrometers and not more than about 10% by weight of said particles being larger than about 1,250 micrometers. Optionally, the percarbonate can be coated with a silicate, borate or water-soluble surfactants. Percarbonate is available from various commercial sources such as FMC, Solvay and Tokai Denka.

While not preferred for the compositions of the present invention which comprise deterative enzymes, the present invention compositions may also comprise as the bleaching agent a chlorine-type bleaching material. Such agents are well known in the art, and include for example sodium dichloroisocyanurate ("NaDCC").

Organic Peroxides, especially Diacyl Peroxides

These are extensively illustrated in Kirk Othmer, Encyclopedia of Chemical Technology, Vol. 17, John Wiley and Sons, 1982 at pages 27-90 and especially at pages 63-72.

If a diacyl peroxide is used, it will preferably be one which exerts minimal adverse impact on spotting/filming. Preferred diacyl peroxides include dibenzoyl peroxide.

Bleach Activators

Preferably, when composition contains a peroxygen bleach component the composition is formulated with an activator (peracid precursor). Preferred activators are selected from the group consisting of tetraacetyl ethylene diamine (TAED), benzoylcaprolactam (BzCL), 4-nitrobenzoylcaprolactam, 3-chlorobenzoylcaprolactam, benzoyloxybenzenesulphonate (BOBS), nonanoyloxybenzenesulphonate (NOBS), phenyl benzoate (PhBz), decanoyloxybenzenesulphonate (C₁₀-OBS), benzoylvalerolactam (BZVL), octanoyloxybenzenesulphonate (C₈-OBS), perhydrolyzable esters and mixtures thereof, most preferably benzoylcaprolactam and benzoylvalerolactam. Particularly preferred bleach activators in the pH range from about 8 to about 9.5 are those selected having an OBS or VL leaving group.

Preferred bleach activators are those described in U.S. Patent 5,130,045, Mitchell et al, and 4,412,934, Chung et al.

The mole ratio of peroxygen bleaching compound (as AvO) to bleach activator in the present invention generally ranges from at least 1:1, preferably from about 20:1 to about 1:1, more preferably from about 10:1 to about 3:1.

Quaternary substituted bleach activators may also be included. The present detergent compositions preferably comprise a quaternary substituted bleach activator (QSBA) or a quaternary substituted peracid (QSP); more preferably, the former. Preferred QSBA structures are further described in U.S. Patent Nos. 5,686,015; 5,460,747; 5,578,136 and 5,584,888.

Levels of bleach activators herein may vary widely, e.g., from about 0.01% to about 90%, by weight of the composition, although lower levels, e.g., more preferably from about 0.1% to about 30%, even more preferably from about 0.1% to about 20%, even more preferably from about 0.5% to about 10%, even more still preferably from about 1% to about 8%, by weight of the composition are more typically used.

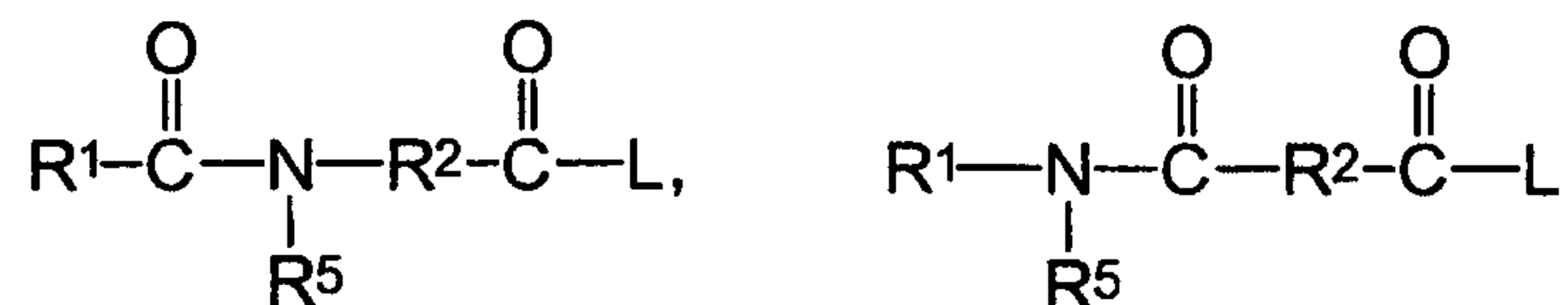
Preferred hydrophilic bleach activators include N,N,N'-tetraacetyl ethylene diamine (TAED) or any of its close relatives including the triacetyl or other unsymmetrical derivatives. TAED and the acetylated carbohydrates such as glucose pentaacetate and tetraacetyl xylose are preferred hydrophilic bleach activators. Depending on the application, acetyl triethyl citrate, a liquid, also has some utility, as does phenyl benzoate.

Preferred hydrophobic bleach activators include substituted amide types described in detail hereinafter, such as activators related to NAPAA, and activators related to certain imidoperacid bleaches, for example as described in U.S. Patent 5,061,807, issued October 29, 1991 and assigned to Hoechst Aktiengesellschaft of Frankfurt, Germany.

Other suitable bleach activators include sodium-4-benzoyloxy benzene sulfonate (SBOBS); sodium-1-methyl-2-benzoyloxy benzene-4-sulphonate; sodium-4-methyl-3-benzoyloxy benzoate (SPCC); trimethyl ammonium toluoyloxy-benzene sulfonate; or sodium 3,5,5-trimethyl hexanoyloxybenzene sulfonate (STHOBS).

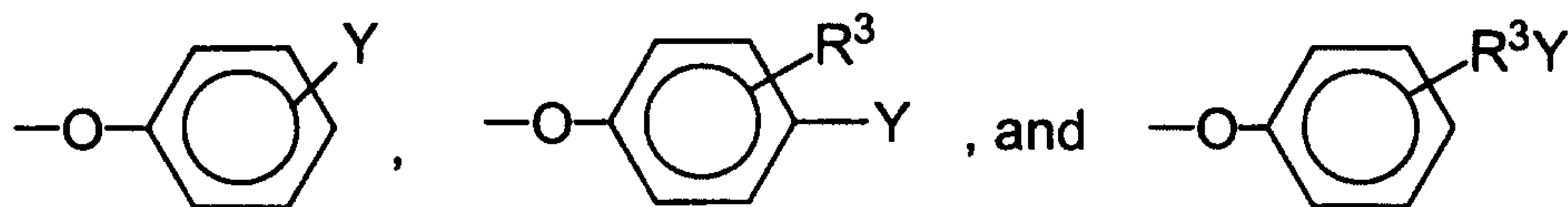
Bleach activators may be used in any amount, typically up to 20%, preferably from 0.1-10% by weight, of the composition, though higher levels, 40% or more, are acceptable, for example in highly concentrated bleach additive product forms or forms intended for appliance automated dosing.

Highly preferred bleach activators useful herein are amide-substituted and have either of the formulae:



or mixtures thereof, wherein R^1 is alkyl, aryl, or alkaryl containing from about 1 to about 14 carbon atoms including both hydrophilic types (short R^1) and hydrophobic types (R^1 is especially from 6, preferably about 8, to about 12), R^2 is alkylene, arylene or alkarylene containing from about 1 to about 14 carbon atoms, R^5 is H, or an alkyl, aryl, or alkaryl containing from about 1 to about 10 carbon atoms, and L is a leaving group which is herein before defined.

Preferred bleach activators also include those of the above general formula wherein L is selected from the group consisting of:



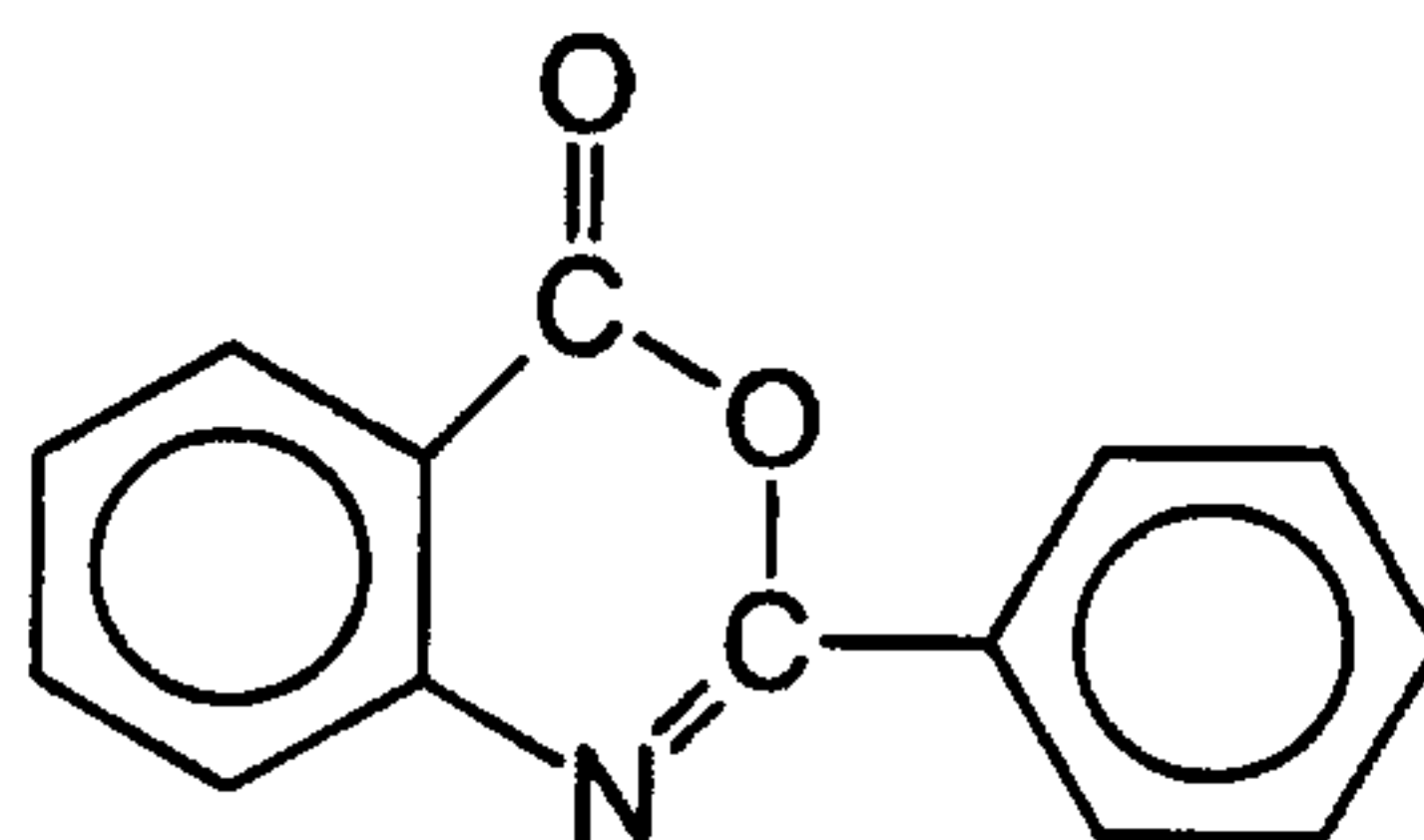
wherein R^3 is as defined above and Y is $-\text{SO}_3^-\text{M}^+$ or $-\text{CO}_2^-\text{M}^+$ wherein M is as defined above.

Preferred examples of bleach activators of the above formulae include:

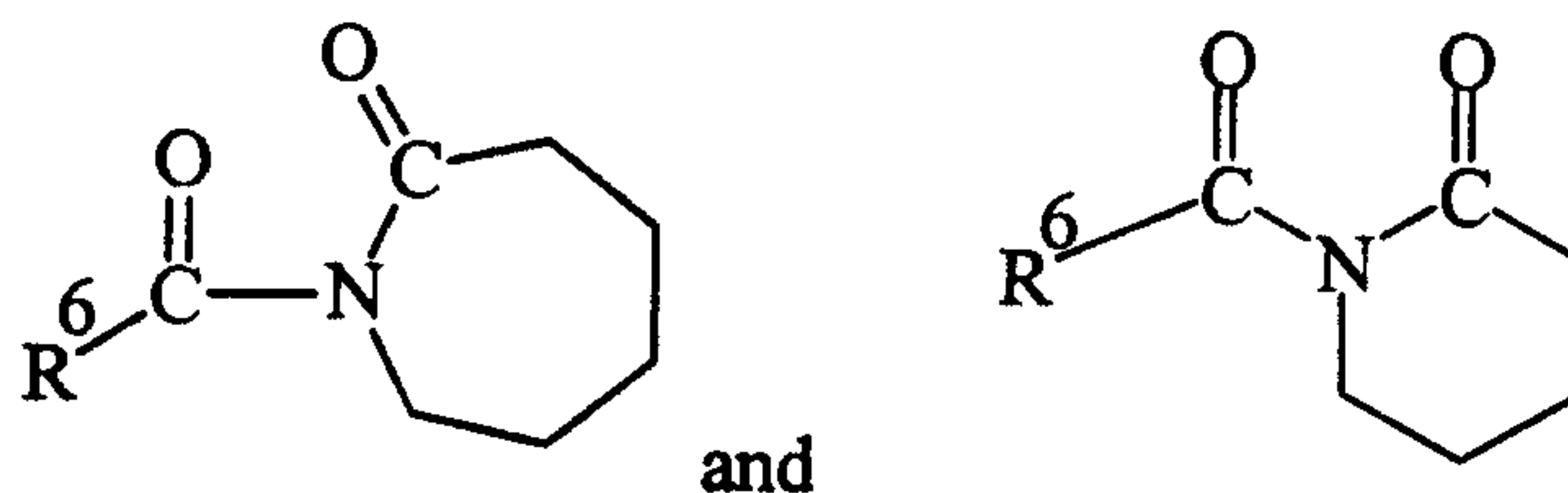
(6-octanamidocaproyl)oxybenzenesulfonate,
(6-nonanamidocaproyl)oxybenzenesulfonate,

(6-decanamidocaproyl)oxybenzenesulfonate, and mixtures thereof.

Other useful activators, disclosed in U.S. 4,966,723, are benzoxazin-type, such as a C₆H₄ ring to which is fused in the 1,2-positions a moiety --C(O)OC(R¹)=N-. A highly preferred activator of the benzoxazin-type is:



Acyl lactam activators are very useful herein, especially the acyl caprolactams (see for example WO 94-28102 A) and acyl valerolactams (see U.S. 5,503,639) of the formulae:



wherein R⁶ is H, alkyl, aryl, alkoxyaryl, an alkaryl group containing from 1 to about 12 carbon atoms, or substituted phenyl containing from about 6 to about 18 carbons. See also U.S. 4,545,784 which discloses acyl caprolactams, including benzoyl caprolactam adsorbed into sodium perborate.

Nonlimiting examples of additional activators useful herein are to be found in U.S. 4,915,854, U.S. 4,412,934 and 4,634,551.

Additional activators useful herein include those of U.S. 5,545,349. Examples include esters of an organic acid and ethylene glycol, diethylene glycol or glycerin, or the acid imide of an organic acid and ethylenediamine; wherein the organic acid is selected from methoxyacetic acid, 2-methoxypropionic acid, p-methoxybenzoic acid, ethoxyacetic acid, 2-ethoxypropionic acid, p-ethoxybenzoic acid, propoxyacetic acid, 2-propoxypropionic acid, p-propoxybenzoic acid, butoxyacetic acid, 2-butoxypropionic acid, p-butoxybenzoic acid, 2-methoxyethoxyacetic acid, 2-methoxy-1-methylethoxyacetic acid, 2-methoxy-2-methylethoxyacetic acid, 2-ethoxyethoxyacetic acid, 2-(2-ethoxyethoxy)propionic acid, p-(2-ethoxyethoxy)benzoic acid, 2-ethoxy-1-

methylethoxyacetic acid, 2-ethoxy-2-methylethoxyacetic acid, 2-propoxyethoxyacetic acid, 2-propoxy-1-methylethoxyacetic acid, 2-propoxy-2-methylethoxyacetic acid, 2-butoxyethoxyacetic acid, 2-butoxy-1-methylethoxyacetic acid, 2-butoxy-2-methylethoxyacetic acid, 2-(2-methoxyethoxy)ethoxyacetic acid, 2-(2-methoxy-1-methylethoxy)ethoxyacetic acid, 2-(2-methoxy-2-methylethoxy)ethoxyacetic acid and 2-(2-ethoxyethoxy)ethoxyacetic acid.

Useful herein as oxygen bleaches are the inorganic peroxides such as Na_2O_2 , superoxides such as KO_2 , organic hydroperoxides such as cumene hydroperoxide and t-butyl hydroperoxide, and the inorganic peroxyacids and their salts such as the peroxosulfuric acid salts, especially the potassium salts of peroxodisulfuric acid and, more preferably, of peroxomonosulfuric acid including the commercial triple-salt form sold as OXONE by DuPont and also any equivalent commercially available forms such as CUROXTM from Akzo or CAROATTM from Degussa. Certain organic peroxides, such as dibenzoyl peroxide, may be useful, especially as additives rather than as primary oxygen bleach.

Mixed oxygen bleach systems are generally useful, as are mixtures of any oxygen bleaches with the known bleach activators, organic catalysts, enzymatic catalysts and mixtures thereof; moreover such mixtures may further include brighteners, photobleaches and dye transfer inhibitors of types well-known in the art.

Other useful peracids and bleach activators herein are in the family of imidoperacids and imido bleach activators. These include phthaloylimidoperoxycaproic acid and related arylimido-substituted and acyloxynitrogen derivatives. For listings of such compounds, preparations and their incorporation into laundry compositions including both granules and liquids, See U.S. 5,487,818; U.S. 5,470,988, U.S. 5,466,825; U.S. 5,419,846; U.S. 5,415,796; U.S. 5,391,324; U.S. 5,328,634; U.S. 5,310,934; U.S. 5,279,757; U.S. 5,246,620; U.S. 5,245,075; U.S. 5,294,362; U.S. 5,423,998; U.S. 5,208,340; U.S. 5,132,431 and U.S. 5,087,385.

Additional bleach activators are those described in U.S. Patent 5,130,045, Mitchell et al, and 4,412,934, Chung et al.

Quaternary substituted bleach activators may also be included. The present detergent compositions preferably comprise a quaternary substituted bleach activator (QSBA) or a quaternary substituted peracid (QSP); more preferably, the former. Preferred QSBA structures are further described in copending U.S. Patent Nos. 5,460,747, 5,584,888 and 5,578,136.

Useful diperoxyacids include, for example, 1,12-diperoxydodecanedioic acid (DPDA); 1,9-diperoxyazelaic acid; diperoxybrassicic acid; diperoxysebasic acid and diperoxyisophthalic acid; 2-decyldiperoxybutane-1,4-dioic acid; and 4,4'-sulphonylbisperoxybenzoic acid. Owing to structures in which two relatively hydrophilic groups are disposed at the ends of the molecule, diperoxyacids have sometimes been classified separately from the hydrophilic and hydrophobic monoperacids, for example as "hydrotropic". Some of the diperacids are hydrophobic in a quite literal sense, especially when they have a long-chain moiety separating the peroxyacid moieties.

It is stressed that if any bleach activators are used then they are limited to ones which cause minimal, preferably no damage to the rubber components in a domestic bleaching process.

Reducing Bleaches

Another class of useful bleaches are the so called reducing bleaches. These are reductants which "reduce", in the electrochemical sense, instead of oxidize as conventional bleaches do.

These are extensively illustrated in Kirk Othmer, Encyclopedia of Chemical Technology, Vol. 17, John Wiley and Sons, 1982.

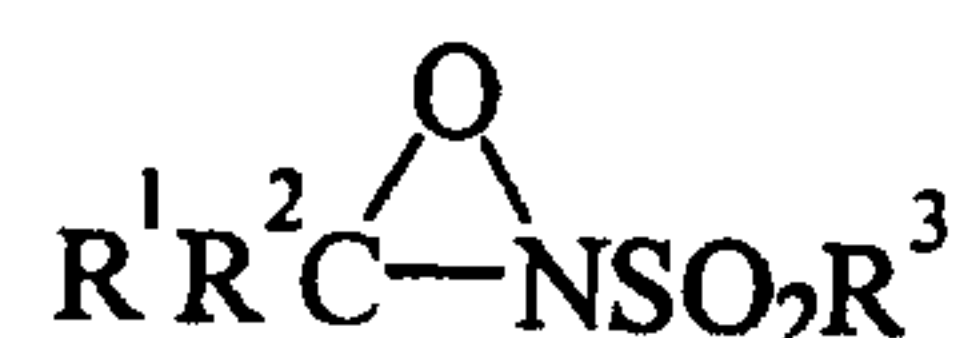
Enzymatic sources of hydrogen peroxide

On a different track from the oxygen bleaching agents illustrated hereinabove, another suitable hydrogen peroxide generating system is a combination of a C₁ -C₄ alkanol oxidase and a C₁ -C₄ alkanol, especially a combination of methanol oxidase

(MOX) and ethanol. Such combinations are disclosed in WO 94/03003. Other enzymatic materials related to bleaching, such as peroxidases, haloperoxidases, oxidases, superoxide dismutases, catalases and their enhancers or, more commonly, inhibitors, may be used as optional ingredients in the instant compositions.

Oxygen transfer agents and precursors

Also useful herein are any of the known organic bleach catalysts, oxygen transfer agents or precursors therefor. These include the compounds themselves and/or their precursors, for example any suitable ketone for production of dioxiranes and/or any of the hetero-atom containing analogs of dioxirane precursors or dioxiranes, such as sulfonimines $R^1R^2C=NSO_2R^3$, see EP 446 982 A, published 1991 and sulfonyloxaziridines, for example:



see EP 446,981 A, published 1991. Preferred examples of such materials include hydrophilic or hydrophobic ketones, used especially in conjunction with monoperoxysulfates to produce dioxiranes in situ, and/or the imines described in U.S. 5,576,282 and references described therein. Oxygen bleaches preferably used in conjunction with such oxygen transfer agents or precursors include percarboxylic acids and salts, percarbonic acids and salts, peroxymonosulfuric acid and salts, and mixtures thereof. See also U.S. 5,360,568; U.S. 5,360,569; and U.S. 5,370,826. In a highly preferred embodiment, the invention relates to a detergent composition which incorporates a transition-metal bleach catalyst in accordance with the invention, and organic bleach catalyst such as one named hereinabove, a primary oxidant such as a hydrogen peroxide source, a hydrophilic bleach activator, and at least one additional detergent, hard-surface cleaner or automatic dishwashing adjunct. Preferred among such compositions are those which further include a precursor for a hydrophobic oxygen bleach such.

Composition pH

Compositions of the invention will have a pH range of from about 2 to about 13, preferably, pH is alkaline, more preferably from about 7 to about 12.5, more preferably

from about 8 to about 12, even more preferably from about 9 to about 11.5. If a composition with a pH greater than 7 is to be more effective, it preferably should contain a buffering agent capable of providing a generally more alkaline pH in the composition and in dilute solutions, i.e., about 0.1% to 0.4% by weight aqueous solution, of the composition. The pKa value of this buffering agent should be about 0.5 to 1.0 pH units below the desired pH value of the composition (determined as described above). Preferably, the pKa of the buffering agent should be from about 7 to about 10. Under these conditions the buffering agent most effectively controls the pH while using the least amount thereof.

The buffering agent may be an active detergent in its own right, or it may be a low molecular weight, organic or inorganic material that is used in this composition solely for maintaining an alkaline pH. Preferred buffering agents for compositions of this invention are nitrogen-containing materials. Some examples are amino acids such as lysine or lower alcohol amines like mono-, di-, and tri-ethanolamine. Other preferred nitrogen-containing buffering agents are Tri(hydroxymethyl)amino methane ($(\text{HOCH}_2)_3\text{CNH}_3$ (TRIS), 2-amino-2-ethyl-1,3-propanediol, 2-amino-2-methyl-propanol, 2-amino-2-methyl-1,3-propanol, disodium glutamate, N-methyl diethanolamide, 1,3-diamino-propanol N,N'-tetra-methyl-1,3-diamino-2-propanol, N,N-bis(2-hydroxyethyl)glycine (bicine) and N-tris (hydroxymethyl)methyl glycine (tricine). Mixtures of any of the above are also acceptable. Useful inorganic buffers/alkalinity sources include the alkali metal carbonates and alkali metal phosphates, e.g., sodium carbonate, sodium polyphosphate. For additional buffers see McCutcheon's EMULSIFIERS AND DETERGENTS, North American Edition, 1997, McCutcheon Division, MC Publishing Company Kirk and WO 95/07971.

The buffering agent, if used, is present in the compositions of the invention herein at a level of from about 0.1% to 15%, preferably from about 1% to 10%, most preferably from about 2% to 8%, by weight of the composition.

Diamines -It is preferred that the diamines used in the present invention are substantially free from impurities. That is, by "substantially free" it is meant that the diamines are over 95% pure, i.e., preferably 97%, more preferably 99%, still more

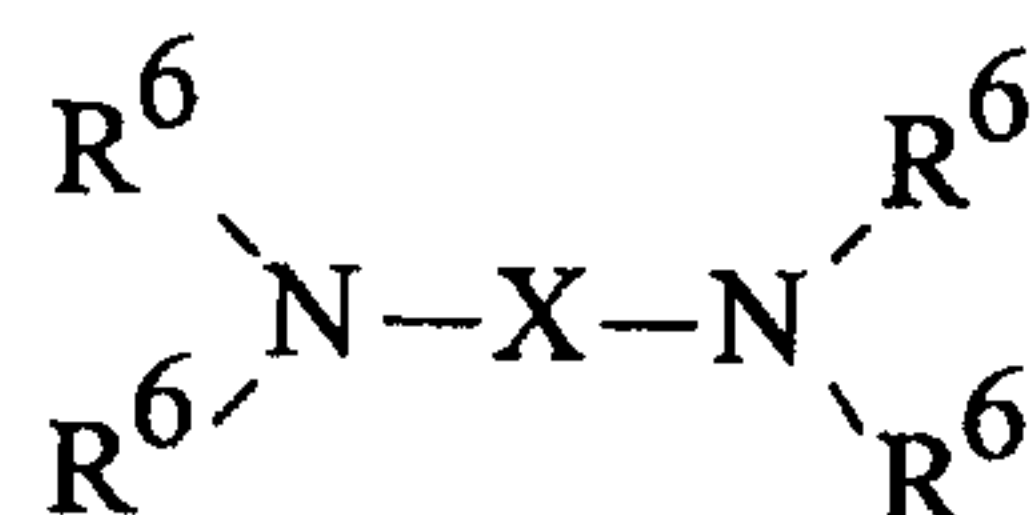
preferably 99.5%, free of impurities. Examples of impurities which may be present in commercially supplied diamines include 2-Methyl-1,3-diaminobutane and alkylhydropyrimidine. Further, it is believed that the diamines should be free of oxidation reactants to avoid diamine degradation and ammonia formation.

It is further preferred that the compositions of the present invention be "malodor" free. That is, that the odor of the headspace does not generate a negative olfactory response from the consumer. This can be achieved in many ways, including the use of perfumes to mask any undesirable odors, the use of stabilizers, such as antioxidants, chelants etc., and/or the use of diamines which are substantially free of impurities. It is believed, without wanting to being limited by theory, that it is the impurities present in the diamines that are the cause of most of the malodors in the compositions of the present invention. These impurities can form during the preparation and storage of the diamines. They can also form during the preparation and storage of the inventive composition. The use of stabilizers such as antioxidants and chelants inhibit and/or prevent the formation of these impurities in the composition from the time of preparation to ultimate use by the consumer and beyond. Hence, it is most preferred to remove, suppress and/or prevent the formation of these malodors by the addition of perfumes, stabilizers and/or the use of diamines which are substantially free from impurities.

Preferred organic diamines are those in which pK1 and pK2 are in the range of about 8.0 to about 11.5, preferably in the range of about 8.4 to about 11, even more preferably from about 8.6 to about 10.75. Preferred materials for performance and supply considerations are 1,3-bis(methylamine)-cyclohexane, 1,3 propane diamine (pK1=10.5; pK2=8.8), 1,6 hexane diamine (pK1=11; pK2=10), 1,3 pentane diamine (Dytek EP) (pK1=10.5; pK2=8.9), 2-methyl 1,5 pentane diamine (Dytek A) (pK1=11.2; pK2=10.0). Other preferred materials are the primary/primary diamines with alkylene spacers ranging from C4 to C8. In general, it is believed that primary diamines are preferred over secondary and tertiary diamines.

Definition of pK1 and pK2 - As used herein, "pKa1" and "pKa2" are quantities of a type collectively known to those skilled in the art as "pKa" pKa is used herein in the same manner as is commonly known to people skilled in the art of chemistry. Values referenced herein can be obtained from literature, such as from "Critical Stability

The diamines useful herein can be defined by the following structure:



wherein each R^6 is independently selected from the group consisting of hydrogen, C_1 - C_4 linear or branched alkyl, alkyleneoxy having the formula:



wherein R^7 is C_2 - C_4 linear or branched alkylene, and mixtures thereof; R^8 is hydrogen, C_1 - C_4 alkyl, and mixtures thereof; m is from 1 to about 10; X is a unit selected from:

- i) C_3 - C_{10} linear alkylene, C_3 - C_{10} branched alkylene, C_3 - C_{10} cyclic alkylene, C_3 - C_{10} branched cyclic alkylene, an alkyleneoxyalkylene having the formula:



wherein R^7 and m are the same as defined herein above;

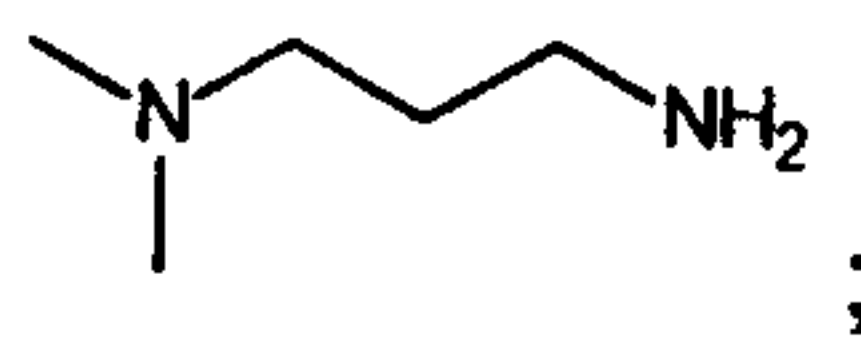
- ii) C_3 - C_{10} linear, C_3 - C_{10} branched linear, C_3 - C_{10} cyclic, C_3 - C_{10} branched cyclic alkylene, C_6 - C_{10} arylene, wherein said unit comprises one or more electron donating or electron withdrawing moieties which provide said diamine with a pK_a greater than about 8; and

- iii) mixtures of (i) and (ii)

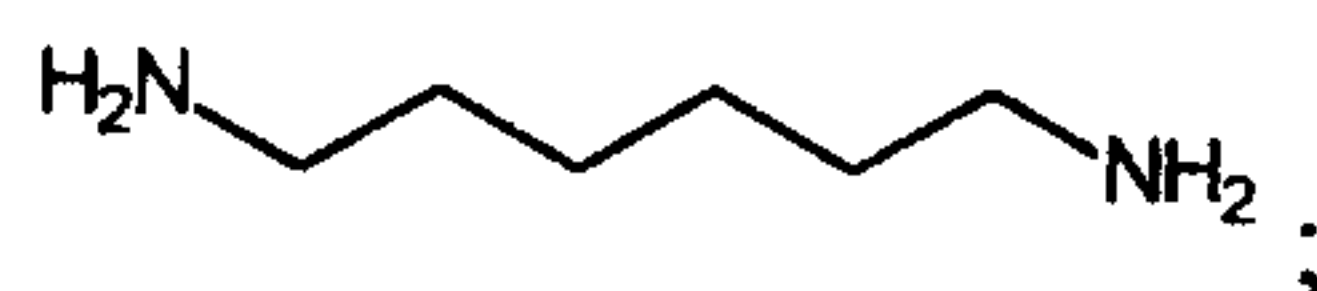
provided said diamine has a pK_a of at least about 8.

Examples of preferred diamines include the following:

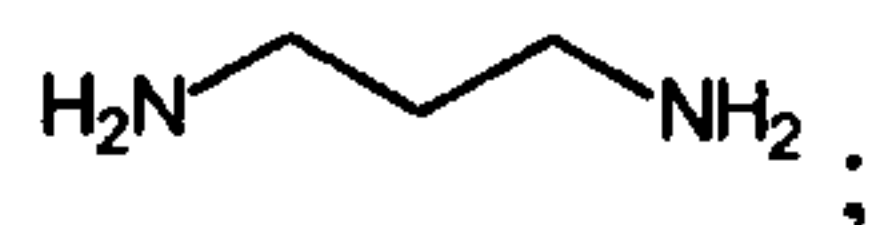
Dimethyl aminopropyl amine:

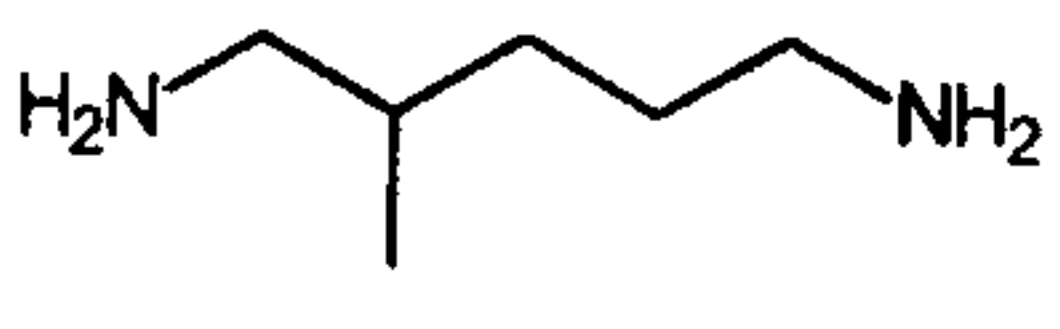


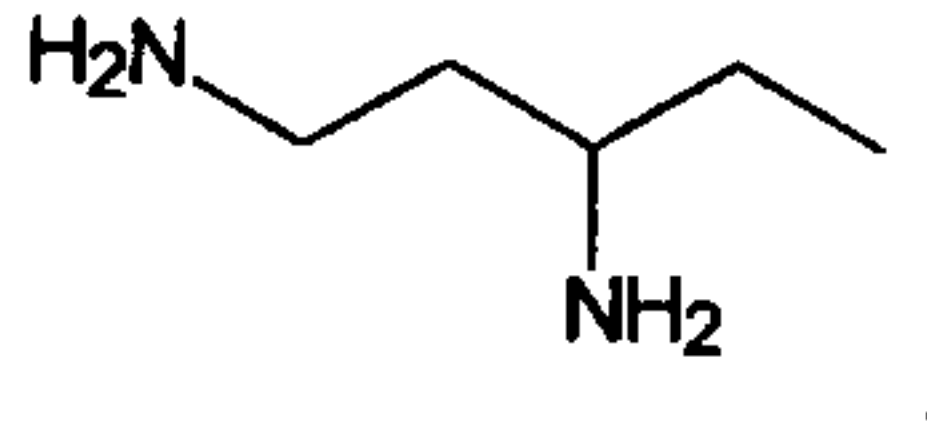
1,6-Hexane Diamine:

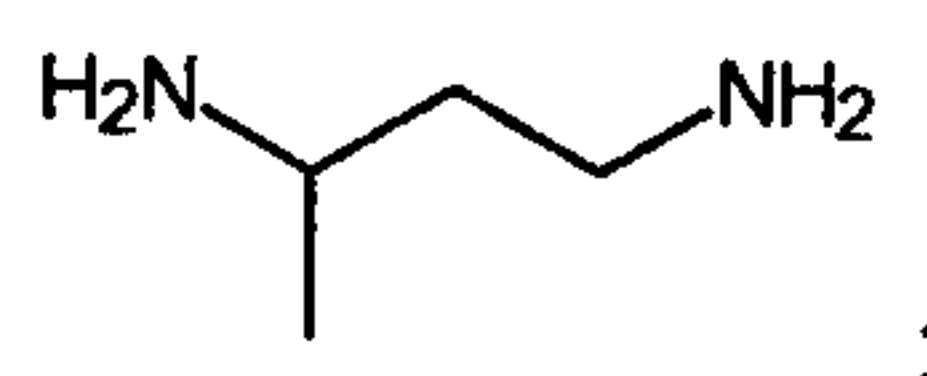


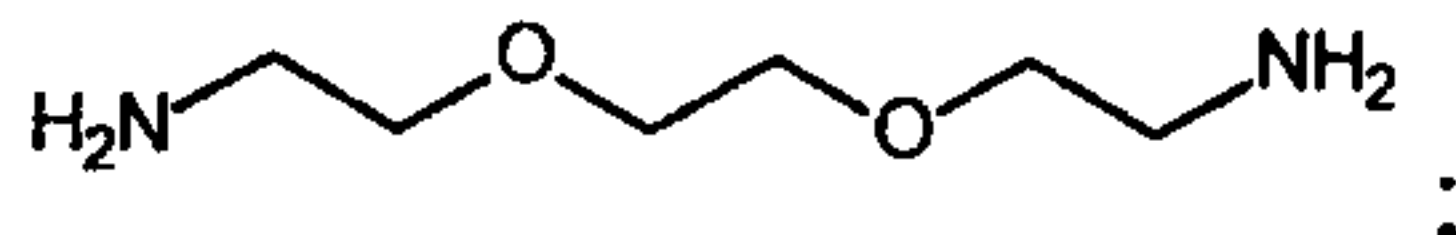
1,3 propane diamine -

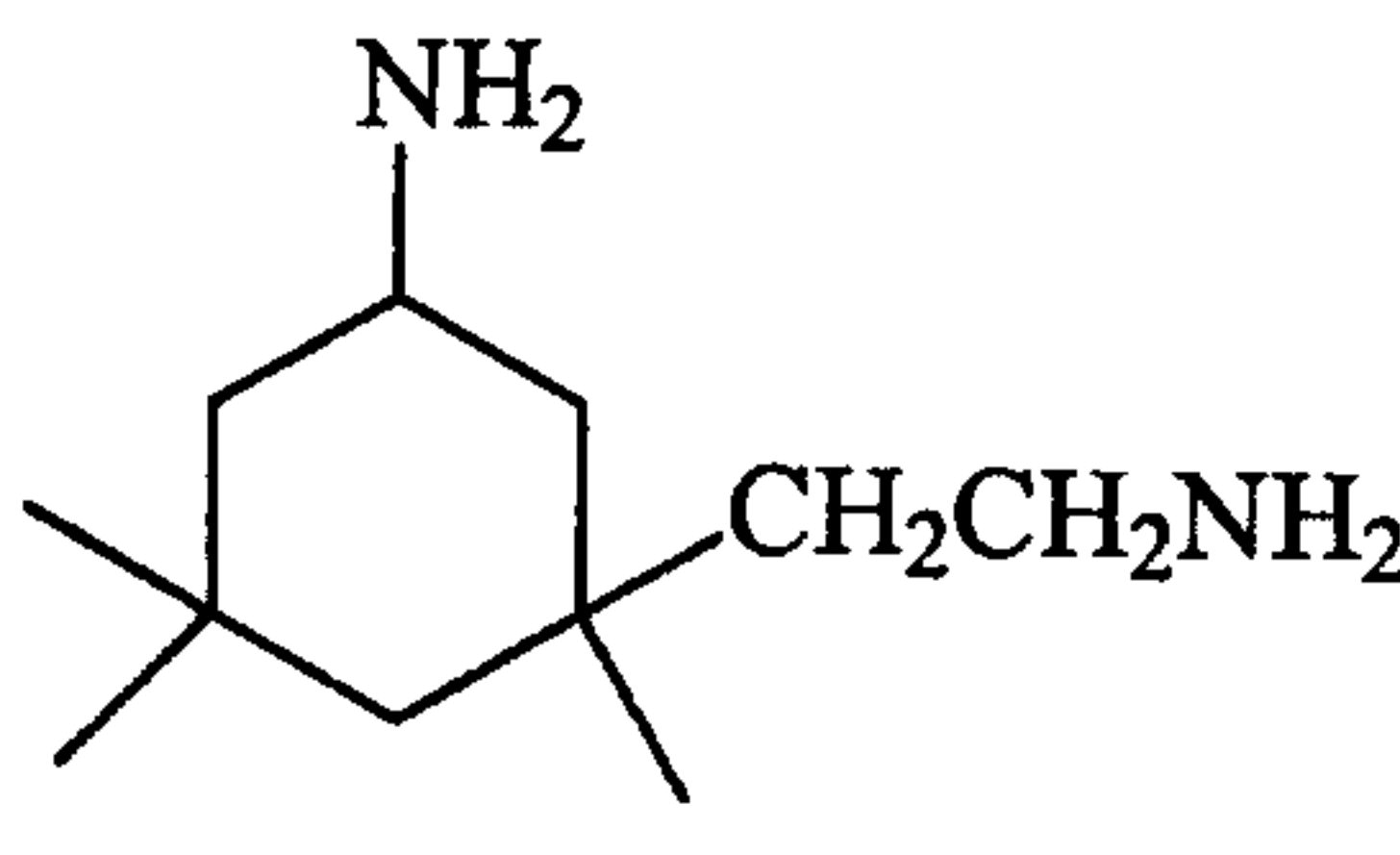


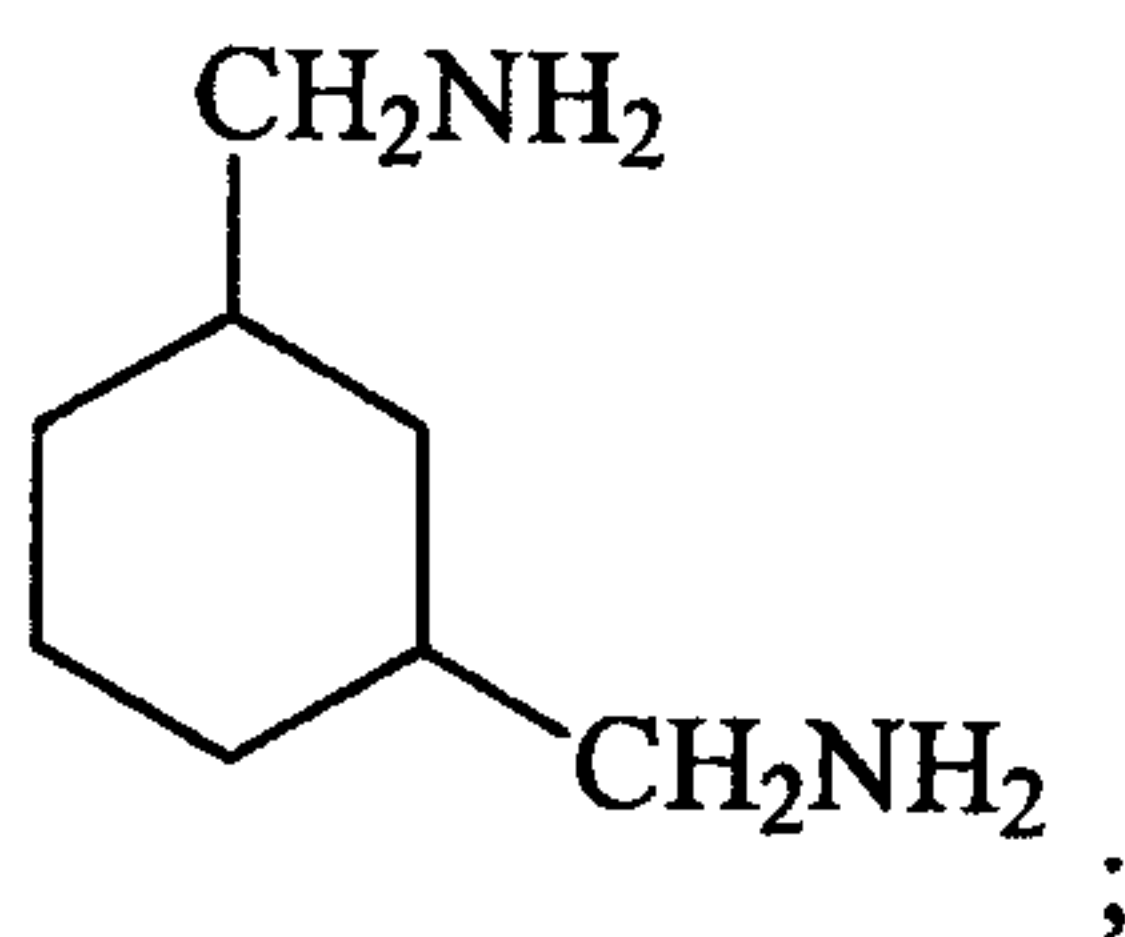
2-methyl 1,5 pentane diamine -  ;

1,3-pentanediamine, available under the tradename Dytek EP  ;

1-methyl-diaminopropane -  ;

Jeffamine EDR 148 -  ;

Isophorone diamine -  ;

1,3-bis(methylamine)-cyclohexane  ;
and mixtures thereof.

Solvents.

Optionally, the compositions of the present invention may further comprise one or more solvents. These solvents may be used in conjunction with an aqueous liquid carrier or they may be used without any aqueous liquid carrier being present. Solvents are broadly defined as compounds that are liquid at temperatures of 20°C-25°C and which are not considered to be surfactants. One of the distinguishing features is that solvents tend to exist as discrete entities rather than as broad mixtures of compounds. Some

solvents which are useful in the hard surface cleaning compositions of the present invention contain from 1 carbon atom to 35 carbon atoms, and contain contiguous linear, branched or cyclic hydrocarbon moieties of no more than 8 carbon atoms. Examples of suitable solvents for the present invention include, methanol, ethanol, propanol, isopropanol, 2-methyl pyrrolidinone, benzyl alcohol and morpholine n-oxide. Preferred among these solvents are methanol and isopropanol.

The compositions used herein may optionally contain an alcohol having a hydrocarbon chain comprising 8 to 18 carbon atoms, preferably 12 to 16. The hydrocarbon chain can be branched or linear, and can be mono, di or polyalcohols. The compositions used herein can optionally comprise from 0.1% to 3% by weight of the total composition of such alcohol, or mixtures thereof, preferably from 0.1% to 1%.

The solvents which can be used herein include all those known to those skilled in the art of hard-surfaces cleaner compositions. Suitable solvents for use herein include ethers and diethers having from 4 to 14 carbon atoms, preferably from 6 to 12 carbon atoms, and more preferably from 8 to 10 carbon atoms. Also other suitable solvents are glycols or alkoxyated glycols, alkoxyated aromatic alcohols, aromatic alcohols, aliphatic branched alcohols, alkoxyated aliphatic branched alcohols, alkoxyated linear C1-C5 alcohols, linear C1-C5 alcohols, C8-C14 alkyl and cycloalkyl hydrocarbons and halohydrocarbons, C6-C16 glycol ethers and mixtures thereof.

Suitable glycols which can be used herein are according to the formula $\text{HO-CR}_1\text{R}_2\text{-OH}$ wherein R_1 and R_2 are independently H or a C2-C10 saturated or unsaturated aliphatic hydrocarbon chain and/or cyclic. Suitable glycols to be used herein are dodecaneglycol and/or propanediol.

Suitable alkoxyated glycols which can be used herein are according to the formula $\text{R-(A)}_n\text{-R}_1\text{-OH}$ wherein R is H, OH, a linear saturated or unsaturated alkyl of from 1 to 20 carbon atoms, preferably from 2 to 15 and more preferably from 2 to 10, wherein R_1 is H or a linear saturated or unsaturated alkyl of from 1 to 20 carbon atoms, preferably from 2 to 15 and more preferably from 2 to 10, and A is an alkoxy group preferably ethoxy, methoxy, and/or propoxy and n is from 1 to 5, preferably 1 to 2. Suitable alkoxyated glycols to be used herein are methoxy octadecanol and/or ethoxyethoxyethanol.

Suitable alkoxyated aromatic alcohols which can be used herein are according to the formula $R(A)_n-OH$ wherein R is an alkyl substituted or non-alkyl substituted aryl group of from 1 to 20 carbon atoms, preferably from 2 to 15 and more preferably from 2 to 10, wherein A is an alkoxy group preferably butoxy, propoxy and/or ethoxy, and n is an integer of from 1 to 5, preferably 1 to 2. Suitable alkoxyated aromatic alcohols are benzoxyethanol and/or benzoxypropanol.

Suitable aromatic alcohols which can be used herein are according to the formula $R-OH$ wherein R is an alkyl substituted or non-alkyl substituted aryl group of from 1 to 20 carbon atoms, preferably from 1 to 15 and more preferably from 1 to 10. For example a suitable aromatic alcohol to be used herein is benzyl alcohol.

Suitable aliphatic branched alcohols which can be used herein are according to the formula $R-OH$ wherein R is a branched saturated or unsaturated alkyl group of from 1 to 20 carbon atoms, preferably from 2 to 15 and more preferably from 5 to 12. Particularly suitable aliphatic branched alcohols to be used herein include 2-ethylbutanol and/or 2-methylbutanol.

Suitable alkoxyated aliphatic branched alcohols which can be used herein are according to the formula $R(A)_n-OH$ wherein R is a branched saturated or unsaturated alkyl group of from 1 to 20 carbon atoms, preferably from 2 to 15 and more preferably from 5 to 12, wherein A is an alkoxy group preferably butoxy, propoxy and/or ethoxy, and n is an integer of from 1 to 5, preferably 1 to 2. Suitable alkoxyated aliphatic branched alcohols include 1-methylpropoxyethanol and/or 2-methylbutoxyethanol.

Suitable alkoxyated linear C1-C5 alcohols which can be used herein are according to the formula $R(A)_n-OH$ wherein R is a linear saturated or unsaturated alkyl group of from 1 to 5 carbon atoms, preferably from 2 to 4, wherein A is an alkoxy group preferably butoxy, propoxy and/or ethoxy, and n is an integer of from 1 to 5, preferably 1 to 2. Suitable alkoxyated aliphatic linear C1-C5 alcohols are butoxy propoxy propanol (n-BPP), butoxyethanol, butoxypropanol, ethoxyethanol or mixtures thereof. Butoxy propoxy propanol is commercially available under the trade mark n-BPP® from Dow chemical.

Suitable linear C1-C5 alcohols which can be used herein are according to the formula $R-OH$ wherein R is a linear saturated or unsaturated alkyl group of from 1 to 5

carbon atoms, preferably from 2 to 4. Suitable linear C1-C5 alcohols are methanol, ethanol, propanol or mixtures thereof.

Other suitable solvents include, but are not limited to, butyl diglycol ether (BDGE), butyltriglycol ether, ter amilic alcohol and the like. Particularly preferred solvents which can be used herein are butoxy propoxy propanol, butyl diglycol ether, benzyl alcohol, butoxypropanol, ethanol, methanol, isopropanol and mixtures thereof.

Typically, the compositions used in the methods of the present invention preferably comprise up to 20% by weight of the total composition of a solvent or mixtures thereof, more preferably from 0.5% to 10%, even more preferably from 3% to 10%. and even more preferably still from 1% to 8%, by weight.

Other suitable solvents for use herein include propylene glycol derivatives such as n-butoxypropanol or n- butoxypropoxypropanol, water-soluble CARBITOL ^R solvents or water-soluble CELLOSOLVE ^R solvents; water-soluble CARBITOL ^R solvents are compounds of the 2-(2-alkoxyethoxy)ethanol class wherein the alkoxy group is derived from ethyl, propyl or butyl; a preferred water-soluble carbitol is 2-(2-butoxyethoxy)ethanol also known as butyl carbitol. Water-soluble CELLOSOLVE ^R solvents are compounds of the 2-alkoxyethoxy ethanol class, with 2-butoxyethoxyethanol being preferred. Other suitable solvents include benzyl alcohol, and diols such as 2-ethyl-1, 3-hexanediol and 2,2,4-trimethyl-1,3-pentanediol and mixtures thereof. Some preferred solvents for use herein are n-butoxypropoxypropanol, BUTYL CARBITOL [®] and mixtures thereof.

The solvents can also be selected from the group of compounds comprising ether derivatives of mono-, di- and tri-ethylene glycol, propylene glycol, butylene glycol ethers, and mixtures thereof. The molecular weights of these solvents are preferably less than 350, more preferably between 100 and 300, even more preferably between 115 and 250. Examples of preferred solvents include, for example, mono-ethylene glycol n-hexyl ether, mono-propylene glycol n-butyl ether, and tri-propylene glycol methyl ether. Ethylene glycol and propylene glycol ethers are commercially available from the Dow Chemical Company under the trade mark "Dowanol" and from the Arco Chemical

Company under the trade mark "Arcosolv". Other preferred solvents including mono- and di-ethylene glycol *n*-hexyl ether are available from the Union Carbide Company.

Hydrophobic Solvent

In order to improve cleaning in liquid compositions, one can use a hydrophobic solvent that has cleaning activity. The hydrophobic solvents which may be employed in the hard surface cleaning compositions herein can be any of the well-known "degreasing" solvents commonly used in, for example, the dry cleaning industry, in the hard surface cleaner industry and the metalworking industry.

A useful definition of such solvents can be derived from the solubility parameters as set forth in "The Hoy," a publication of Union Carbide.

The most useful parameter appears to be the hydrogen bonding parameter which is calculated by the formula:

$$\gamma_H = \gamma_T \left[\frac{\alpha - 1}{\alpha} \right]^{1/2}$$

wherein γ_H is the hydrogen bonding parameter, α is the aggregation number,

$$(\text{Log } \alpha = 3.39066 \frac{T_b}{T_c} - 0.15848 - \text{Log } M), \text{ and}$$

d

γ_T is the solubility parameter which is obtained from the formula:

$$\gamma_T = \left[\frac{(\Delta H_{25} - RT)d}{M} \right]^{1/2}$$

where ΔH_{25} is the heat of vaporization at 25°C, R is the gas constant (1.987 cal/mole/deg), T is the absolute temperature in °K, T_b is the boiling point in °K, T_c is the critical temperature in °K, d is the density in g/ml, and M is the molecular weight.

For the compositions herein, hydrogen bonding parameters are preferably less than 7.7, more preferably from 2 to 7, or 7.7, and even more preferably from 3 to 6. Solvents with lower numbers become increasingly difficult to solubilize in the compositions and have a greater tendency to cause a haze on glass. Higher numbers require more solvent to provide good greasy/oily soil cleaning.

Hydrophobic solvents are typically used, when present, at a level of from 0.5% to 30%, preferably from 2% to 15%, more preferably from 3% to 8%. Dilute compositions typically have solvents at a level of from 1% to 10%, preferably from 3% to 6%. Concentrated compositions contain from 10% to 30%, preferably from 10% to 20% of solvent.

Many of such solvents comprise hydrocarbon or halogenated hydrocarbon moieties of the alkyl or cycloalkyl type, and have a boiling point well above room temperature, i.e., above 20°C.

One highly preferred solvent is limonene, which not only has good grease removal but also a pleasant odor properties.

The formulator of compositions of the present type will be guided in the selection of solvent partly by the need to provide good grease-cutting properties, and partly by aesthetic considerations. For example, kerosene hydrocarbons function quite well for grease cutting in the present compositions, but can be malodorous. Kerosene must be exceptionally clean before it can be used, even in commercial situations. For home use, where malodors would not be tolerated, the formulator would be more likely to select solvents which have a relatively pleasant odor, or odors which can be reasonably modified by perfuming.

The C₆-C₉ alkyl aromatic solvents, especially the C₆-C₉ alkyl benzenes, preferably octyl benzene, exhibit excellent grease removal properties and have a low, pleasant odor. Likewise, the olefin solvents having a boiling point of at least 100°C, especially alpha-olefins, preferably 1-decene or 1-dodecene, are excellent grease removal solvents.

Generically, glycol ethers useful herein have the formula $R^{11}O-(R^{12}O)_mH$ wherein each R¹¹ is an alkyl group which contains from 3 to 8 carbon atoms, each R¹² is either ethylene or propylene, and m¹ is a number from 1 to 3. The most preferred glycol ethers are selected from the group consisting of monopropyleneglycolmonopropyl ether, dipropyleneglycolmonobutyl ether, monopropyleneglycolmonobutyl ether, ethyleneglycolmonohexyl ether, ethyleneglycolmonobutyl ether,

diethyleneglycolmonoethyl ether, monoethyleneglycolmonoethyl ether, monoethyleneglycolmonobutyl ether, and mixtures thereof.

A particularly preferred type of solvent for these hard surface cleaner compositions comprises diols having from 6 to 16 carbon atoms in their molecular structure. Preferred diol solvents have a solubility in water of from 0.1 to 20 g/100 g of water at 20°C. The diol solvents in addition to good grease cutting ability, impart to the compositions an enhanced ability to remove calcium soap soils from surfaces such as bathtub and shower stall walls. These soils are particularly difficult to remove, especially for compositions which do not contain an abrasive. Other solvents such as benzyl alcohol, n-hexanol, and phthalic acid esters of C₁₋₄ alcohols can also be used.

Solvents such as pine oil, orange terpene, benzyl alcohol, n-hexanol, phthalic acid esters of C₁₋₄ alcohols, butoxy propanol, Butyl Carbitol® and 1(2-n-butoxy-1-methylethoxy)propane-2-ol (also called butoxy propoxy propanol or dipropylene glycol monobutyl ether), hexyl diglycol (Hexyl Carbitol®), butyl triglycol, diols such as 2,2,4-trimethyl-1,3-pentanediol, and mixtures thereof, can be used. The butoxy-propanol solvent should have no more than 20%, preferably no more than 10%, more preferably no more than 7%, of the secondary isomer in which the butoxy group is attached to the secondary atom of the propanol for improved odor.

The level of hydrophobic solvent is preferably, when present, from 1% to 15%, more preferably from 2% to 12%, even more preferably from 5% to 10%.

Hydrotropes

The compositions used in the methods of the present invention may optionally comprise one or more materials which are hydrotropes. Hydrotropes suitable for use in the compositions herein include the C₁-C₃ alkyl aryl sulfonates, C₆-C₁₂ alkanols, C₁-C₆ carboxylic sulfates and sulfonates, urea, C₁-C₆ hydrocarboxylates, C₁-C₄ carboxylates, C₂-C₄ organic diacids and mixtures of these hydrotrope materials. The composition of the present invention preferably comprises from 0.5% to 8%, by weight of the liquid detergent composition of a hydrotrope selected from alkali metal and calcium xylene and toluene sulfonates.

Suitable C₁-C₃ alkyl aryl sulfonates include sodium, potassium, calcium and ammonium xylene sulfonates; sodium, potassium, calcium and ammonium toluene sulfonates; sodium, potassium, calcium and ammonium cumene sulfonates; and sodium, potassium, calcium and ammonium substituted or unsubstituted naphthalene sulfonates and mixtures thereof.

Suitable C₁-C₈ carboxylic sulfate or sulfonate salts are any water soluble salts or organic compounds comprising 1 to 8 carbon atoms (exclusive of substituent groups), which are substituted with sulfate or sulfonate and have at least one carboxylic group. The substituted organic compound may be cyclic, acyclic or aromatic, i.e. benzene derivatives. Preferred alkyl compounds have from 1 to 4 carbon atoms substituted with sulfate or sulfonate and have from 1 to 2 carboxylic groups. Examples of this type of hydrotrope include sulfosuccinate salts, sulfophthalic salts, sulfoacetic salts, m-sulfobenzoic acid salts and diester sulfosuccinates, preferably the sodium or potassium salts as disclosed in U.S. 3,915,903.

Suitable C₁-C₄ hydrocarboxylates and C₁-C₄ carboxylates for use herein include acetates and propionates and citrates. Suitable C₂-C₄ diacids for use herein include succinic, glutaric and adipic acids.

Other compounds which deliver hydrotropic effects suitable for use herein as a hydrotrope include C₆-C₁₂ alkanols and urea.

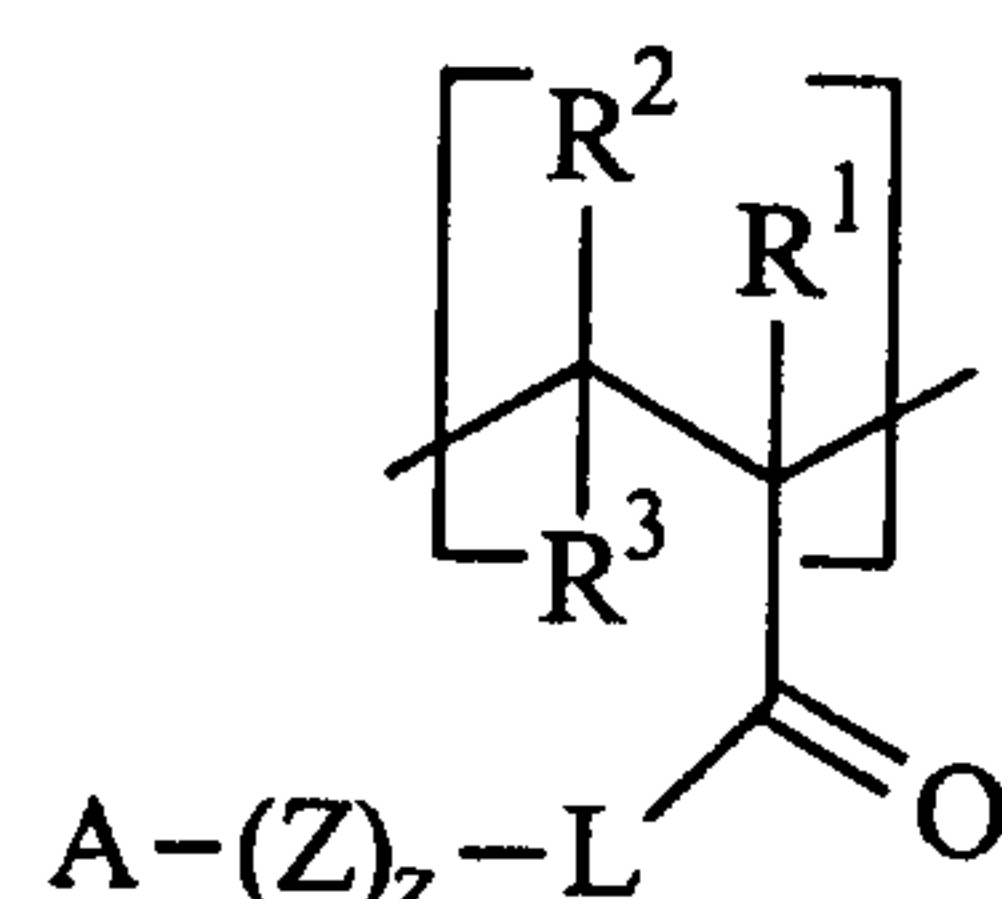
Preferred hydrotropes for use herein are sodium, potassium, calcium and ammonium cumene sulfonate; sodium, potassium, calcium and ammonium xylene sulfonate; sodium, potassium, calcium and ammonium toluene sulfonate and mixtures thereof. Most preferred are sodium cumene sulfonate and calcium xylene sulfonate and mixtures thereof. These preferred hydrotrope materials can be present in the composition to the extent of from 0.5% to 8% by weight.

Polymeric Suds Stabilizers

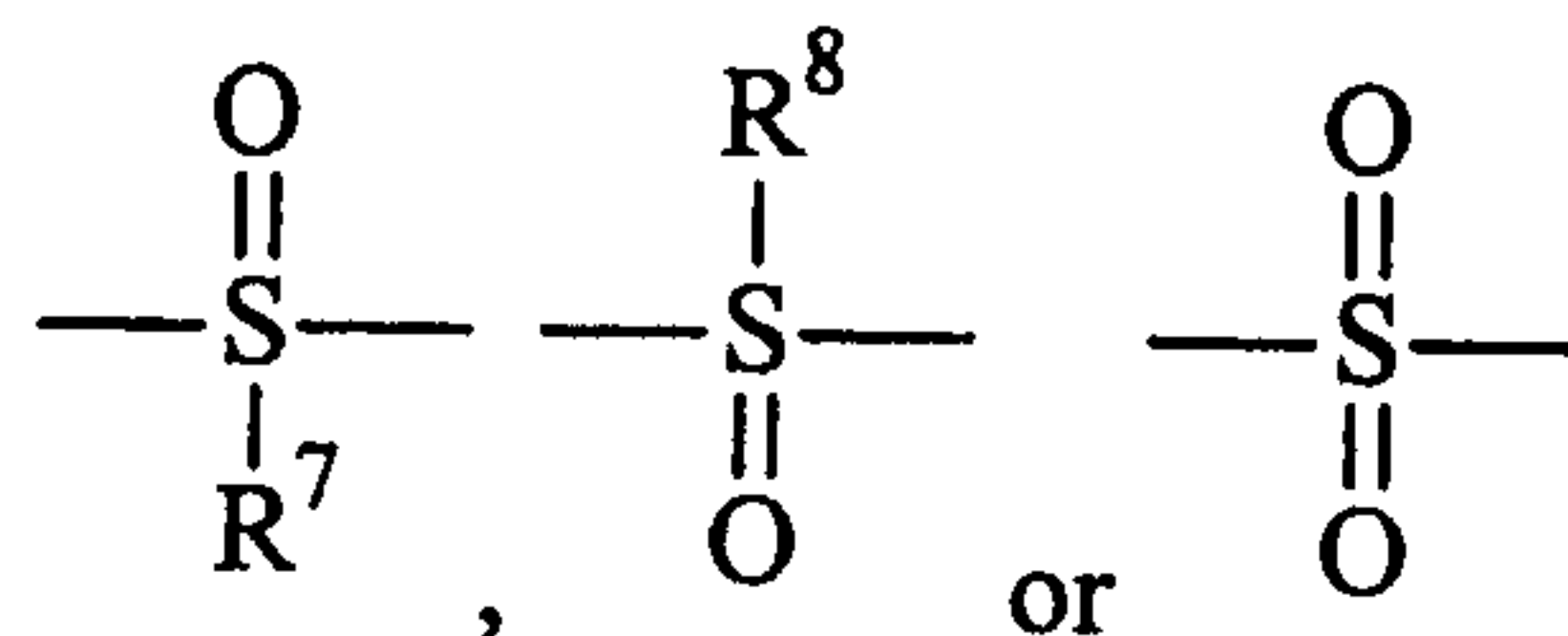
The compositions of the present invention may also contain a polymeric suds stabilizer. The compositions preferably comprise at least an effective amount of the polymeric suds stabilizers described herein, more preferably from about 0.01% to about 10%, even more preferably from about 0.05% to about 5%, even more preferably still

preferably from about 0.1% to about 2% by weight, of said composition. What is meant herein by "an effective amount polymeric suds stabilizers " is that the suds volume and suds duration produced by the presently described compositions are sustained for an increased amount of time relative to a composition which does not comprise one or more of the polymeric suds stabilizer described herein. Additionally, the polymeric suds stabilizer can be present as the free base or as a salt. Typical counter ions include, citrate, maleate, sulfate, chloride, etc.

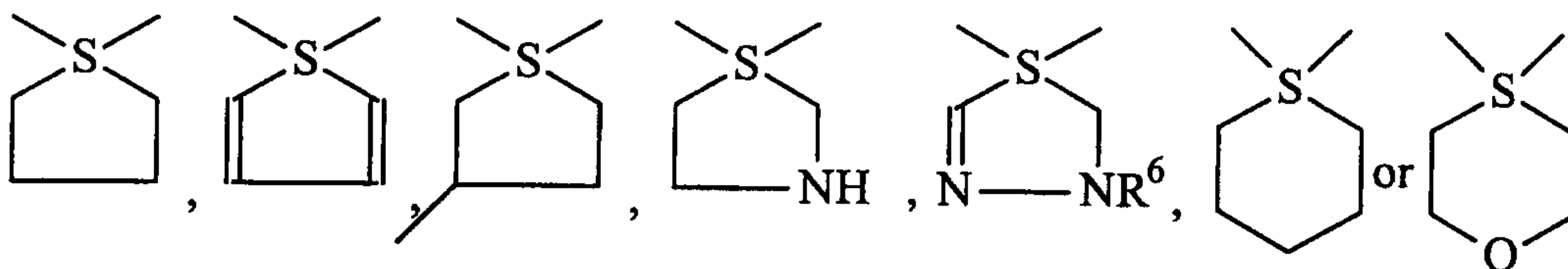
One preferred polymeric suds stabilizer are polymers comprising at least one monomeric unit of the formula:



wherein each of R^1 , R^2 and R^3 are independently selected from the group consisting of hydrogen, C_1 to C_6 alkyl, and mixtures thereof, preferably hydrogen, C_1 to C_3 alkyl, more preferably, hydrogen or methyl. L is selected from the group consisting of a bond, O, NR^6 , SR^7R^8 and mixtures thereof, preferably, O, NR^6 , wherein R^6 is selected from the group consisting of hydrogen, C_1 to C_8 alkyl and mixtures thereof, preferably, hydrogen, C_1 to C_3 , and mixtures thereof, more preferably hydrogen, methyl; each of R^7 and R^8 are independently hydrogen, O, C_1 to C_8 alkyl and mixtures thereof, preferably, hydrogen, C_1 to C_3 , and mixtures thereof, more preferably hydrogen or methyl. By "O", an oxygen linked via a double bond is meant, such as a carbonyl group. Furthermore this means that when either or both R^7R^8 is "O", SR^7R^8 can have the following structures:

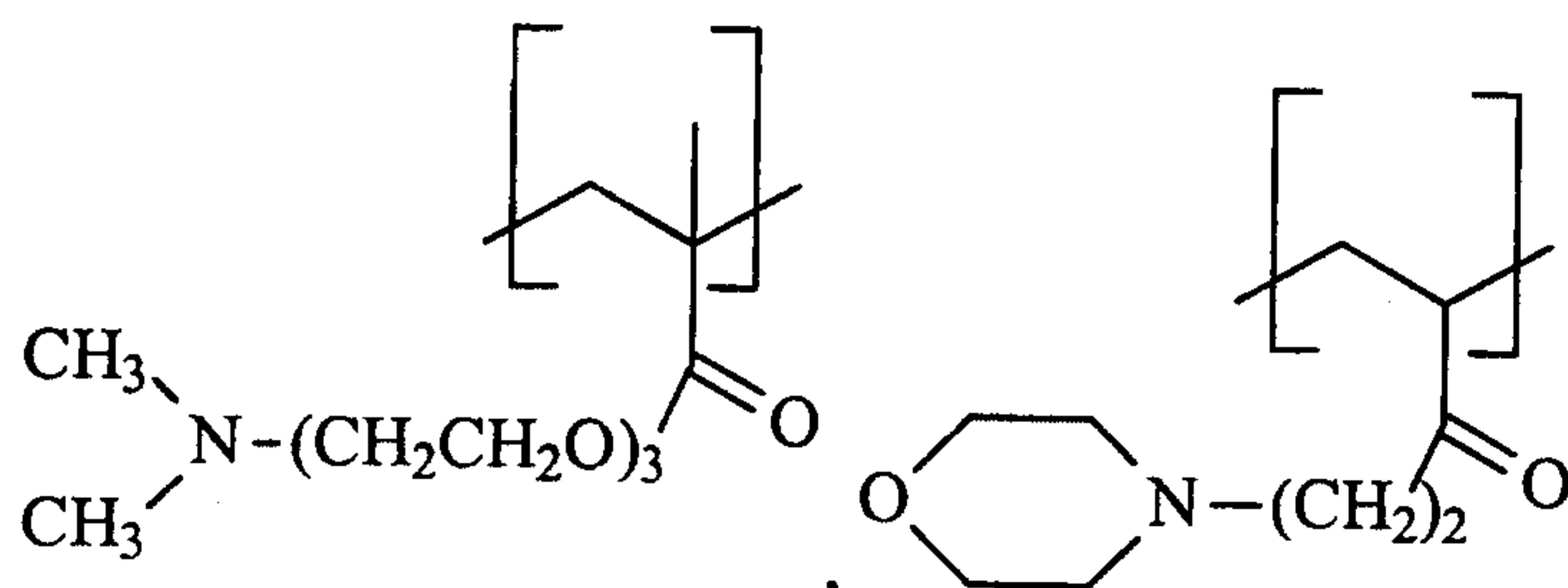


Alternatively, SR^7R^8 form a heterocyclic ring containing from 4 to 7 carbon atoms, optionally containing additional hetero atoms and optionally substituted. For example SR^7R^8 can be:

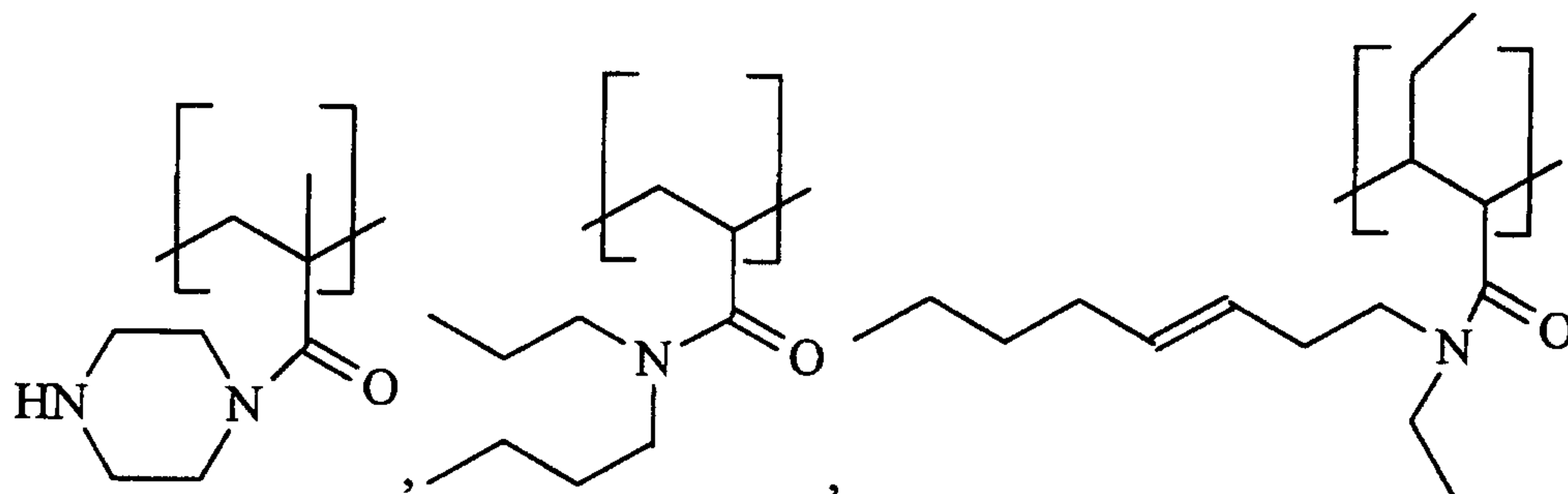


However, it is preferred that SR^7R^8 , when present, is not a heterocycle.

When L is a bond it means that there is a direct link, or a bond, between the carbonyl carbon atom to Z, when z is not zero. For example:

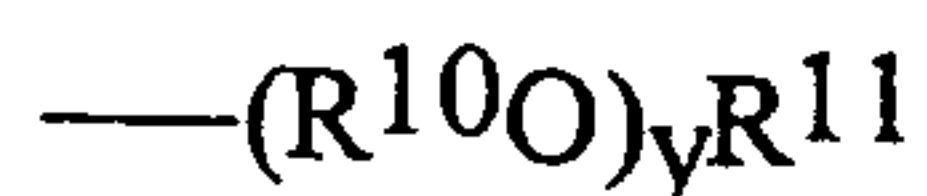


When L is a bond and z is zero, it means L is a bond from the carbonyl atom to A. For example:



Z is selected from the group consisting of: $-(CH_2)-$, $(CH_2-CH=CH)-$, $-(CH_2-CHOH)-$, $(CH_2-CHNR^6)-$, $-(CH_2-CHR^{14}-O)-$ and mixtures thereof, preferably $-(CH_2)-$. R^{14} is selected from the group consisting of hydrogen, C_1 to C_6 alkyl and mixtures thereof, preferably hydrogen, methyl, ethyl and mixtures thereof; z is an integer selected from about 0 to about 12, preferably about 2 to about 10, more preferably about 2 to about 6.

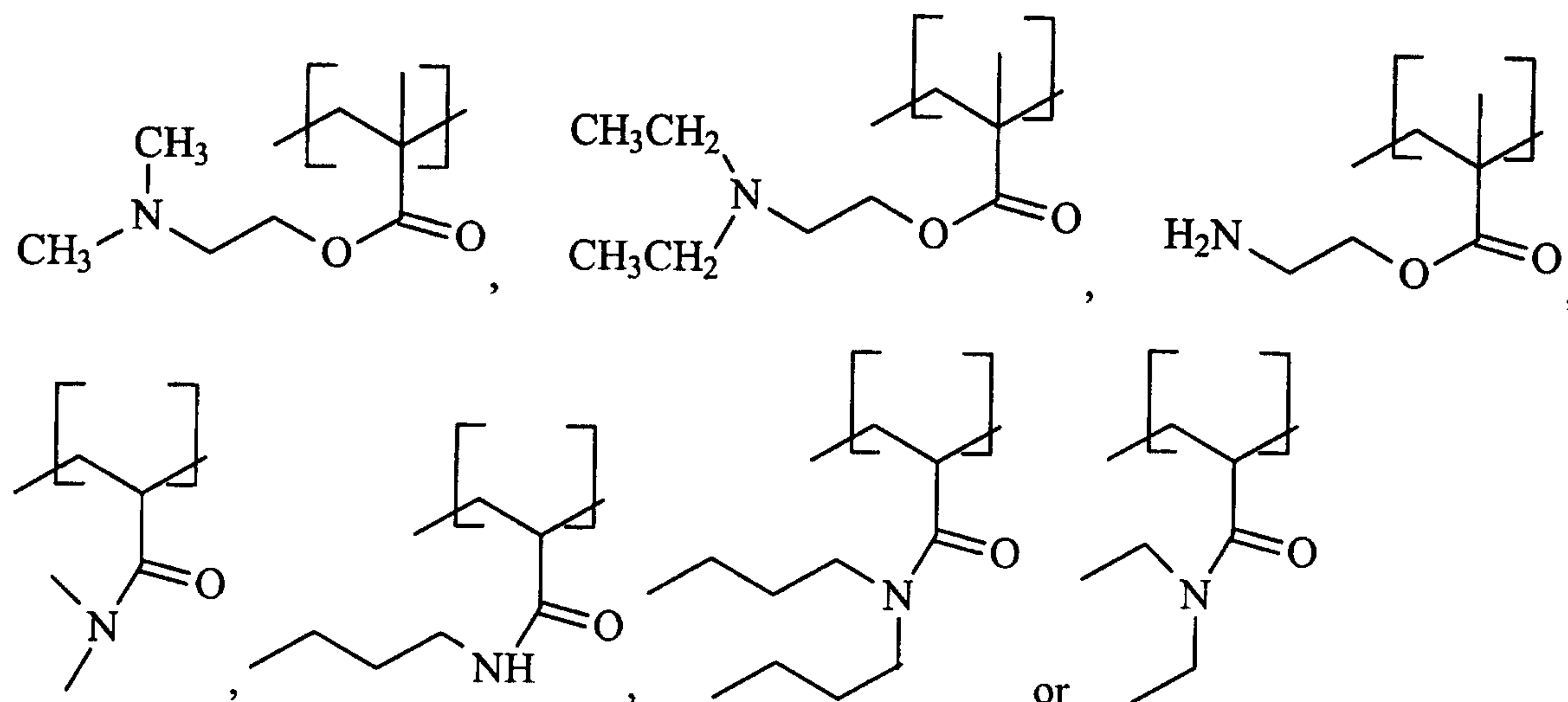
A is NR^4R^5 . Wherein each of R^4 and R^5 are independently selected from the group consisting of hydrogen, C_1 - C_8 linear or branched alkyl, alkyleneoxy having the formula:



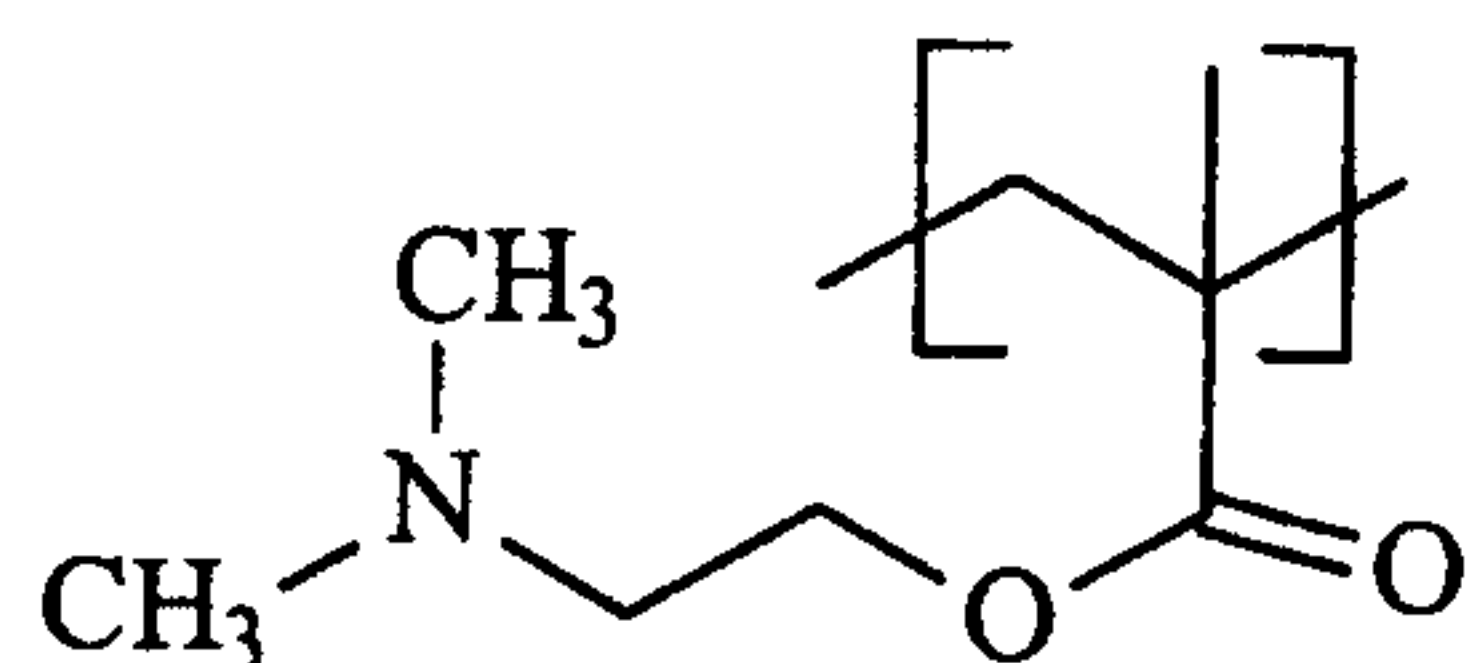
wherein R^{10} is C_2 - C_4 linear or branched alkylene, and mixtures thereof; R^{11} is hydrogen, C_1 - C_4 alkyl, and mixtures thereof; y is from 1 to about 10. Preferably R^4 and R^5 are independently, hydrogen, C_1 to C_4 alkyl. Alternatively, NR^4R^5 can form a heterocyclic ring containing from 4 to 7 carbon atoms, optionally containing additional hetero atoms, optionally fused to a benzene ring, and optionally substituted by C_1 to C_8 hydrocarbonyl. Examples of suitable heterocycles, both substituted and unsubstituted, are indolyl, isoindolyl, imidazolyl, imidazolyl, piperidinyl, pyrazolyl, pyrazolyl, pyridinyl, piperazinyl, pyrrolidinyl, pyrrolidinyl, guanidino, amidino, quinidinyl, thiazolyl, morpholine and mixtures thereof, with morpholino and piperazinyl being preferred. Furthermore the polymeric suds stabilizer has a molecular weight of from about 1,000 to about 2,000,000 preferably from about 5,000 to about 1,000,000, more preferably from about 10,000 to about 750,000, more preferably from about 20,000 to about 500,000, even more preferably from about 35,000 to about 300,000 daltons. The molecular weight of the polymeric suds boosters, can be determined via conventional gel permeation chromatography.

While, it is preferred that the polymeric suds stabilizers be selected from homopolymer, copolymers and terpolymers, other polymers (or multimers) of the at least one monomeric unit, the polymeric suds stabilizers can also be envisioned via polymerization of the at least one monomeric unit with a wider selection of monomers. That is, all the polymeric suds stabilizers can be a homopolymers, copolymers, terpolymers, etc. of the at least one monomeric unit, or the polymeric suds stabilizer can be copolymers, terpolymers, etc. containing one, two or more of the at least one monomeric unit and one, two or more monomeric units other than the at least one monomeric unit. In the copolymer, terpolymer, etc., the distribution of the monomers can be either random or repeating.

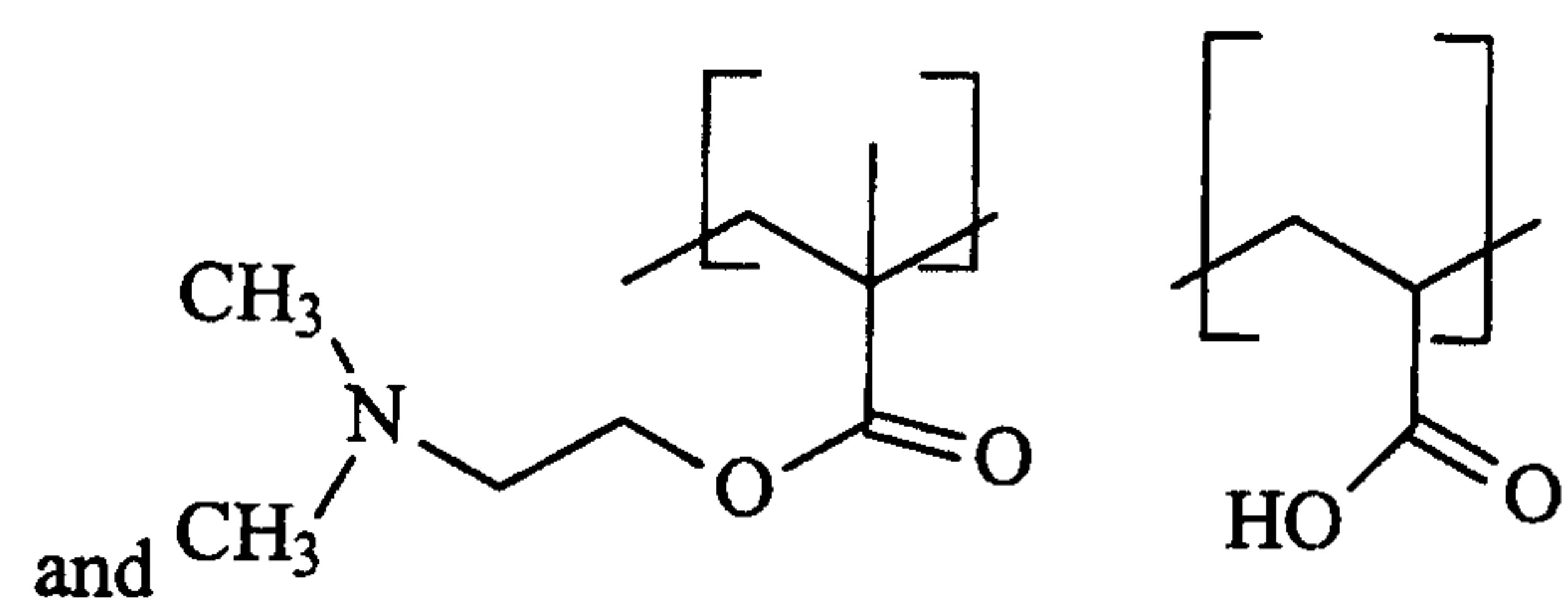
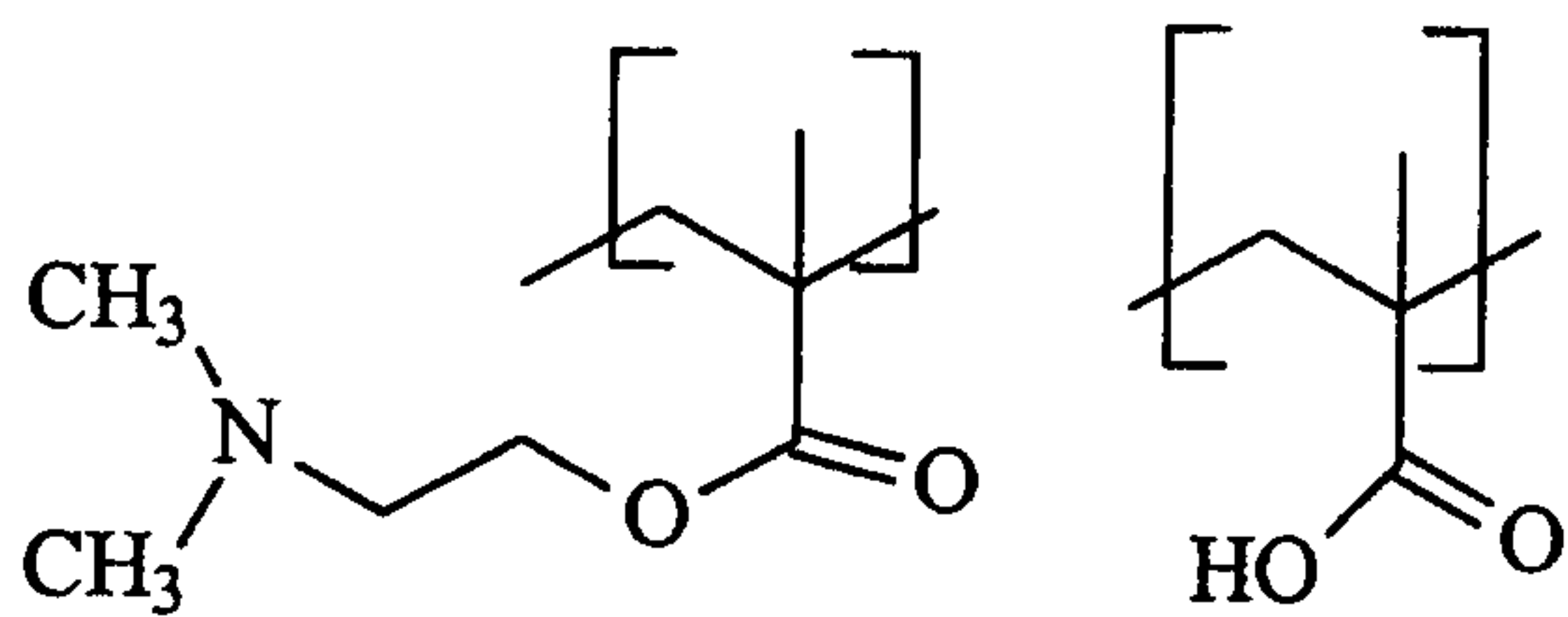
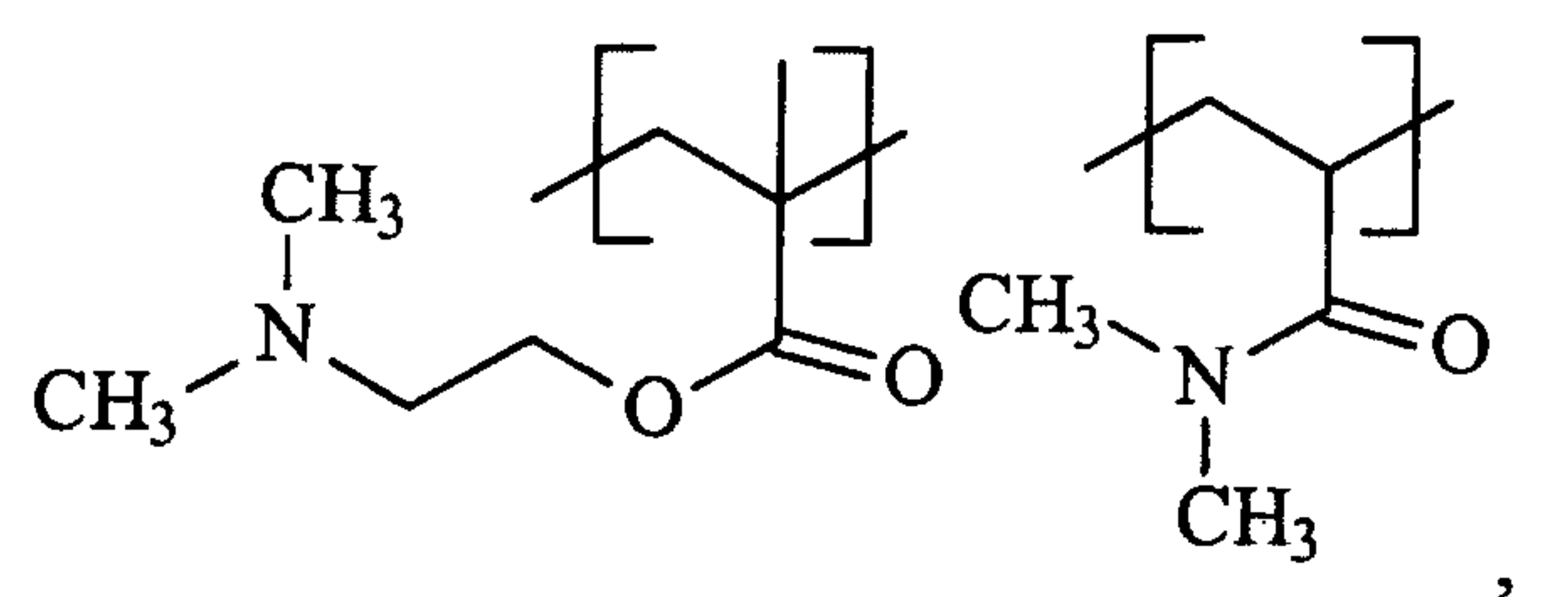
Some preferred suds stabilizing polymers are homopolymers, copolymers or terpolymers which comprise at least one monomeric units, selected from:



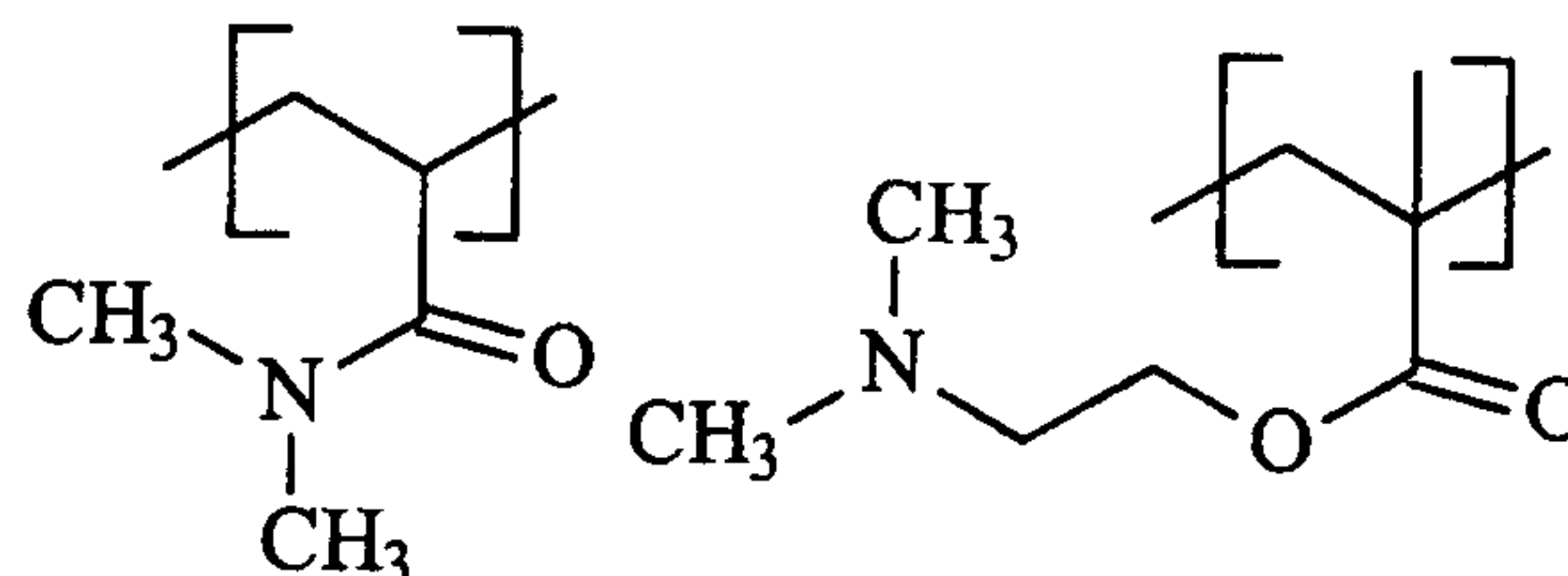
An example of a preferred homopolymer is 2-dimethylaminoethyl methacrylate (DMAM) having the formula:



Some preferred copolymers include:
copolymers of

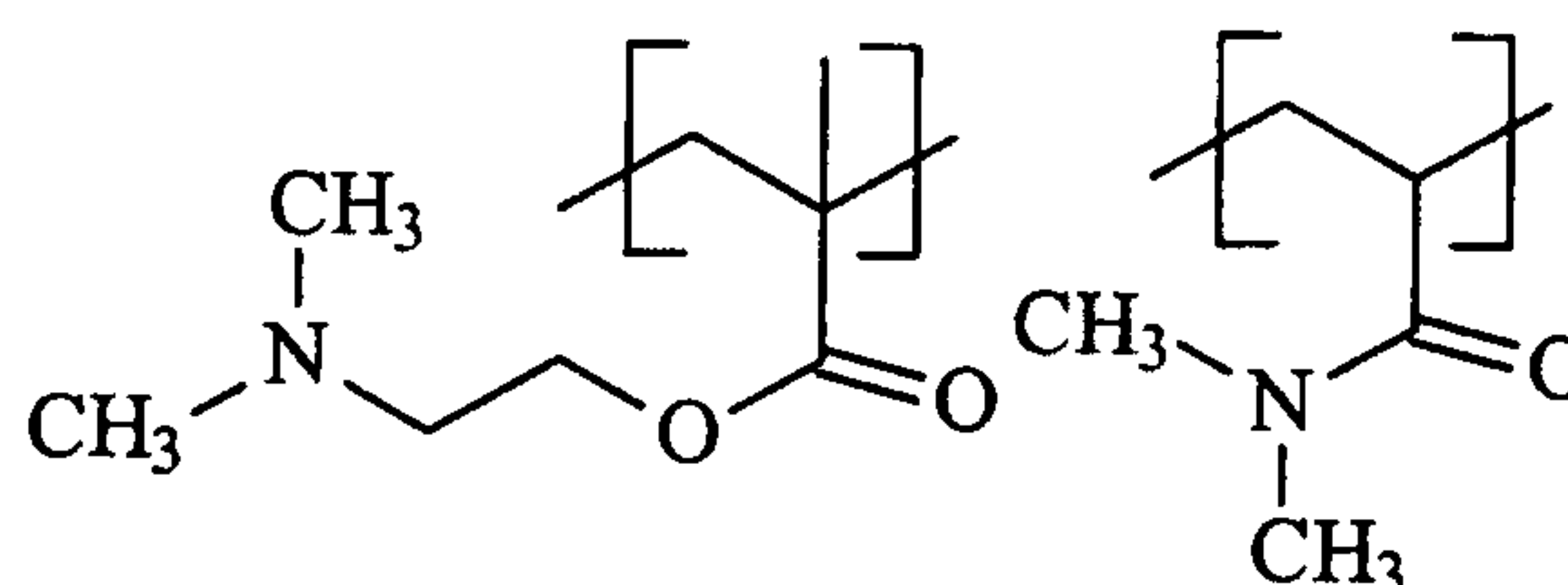


An example of a preferred copolymer is the (DMA)/(DMAM) copolymer having the general formula:



wherein the ratio of (DMA) to (DMAM) is about 1 to about 10, preferably about 1 to about 5, more preferably about 1 to about 3.

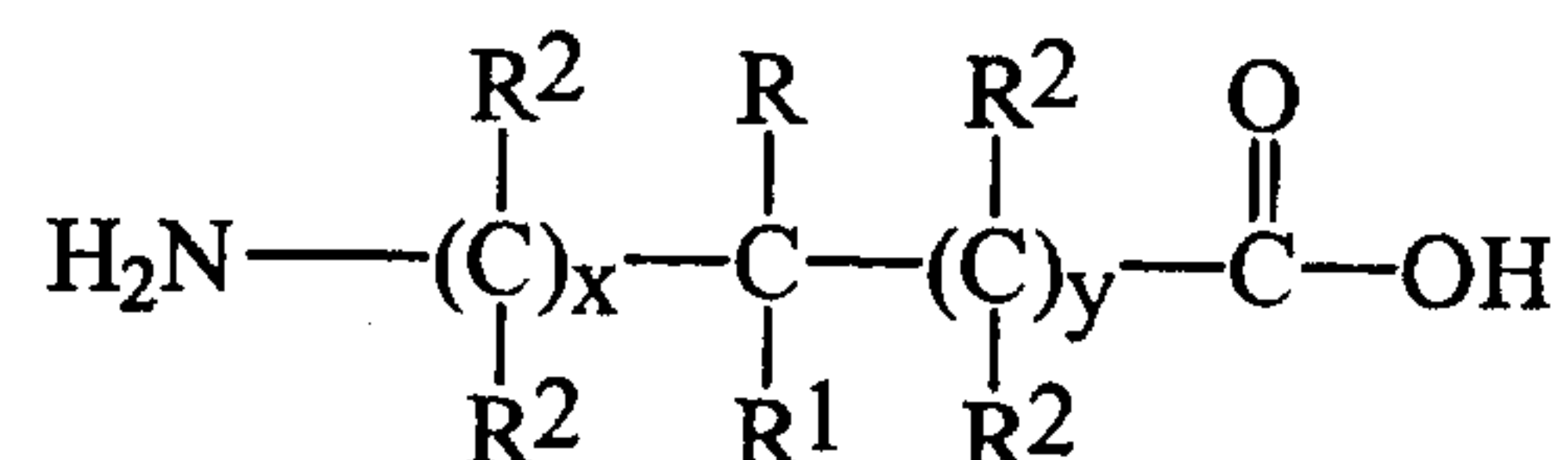
An example of a preferred copolymer is the (DMAM)/(DMA) copolymer having the general formula:



wherein the ratio of (DMAM) to (DMA) is about 1 to about 5, preferably about 1 to about 3.

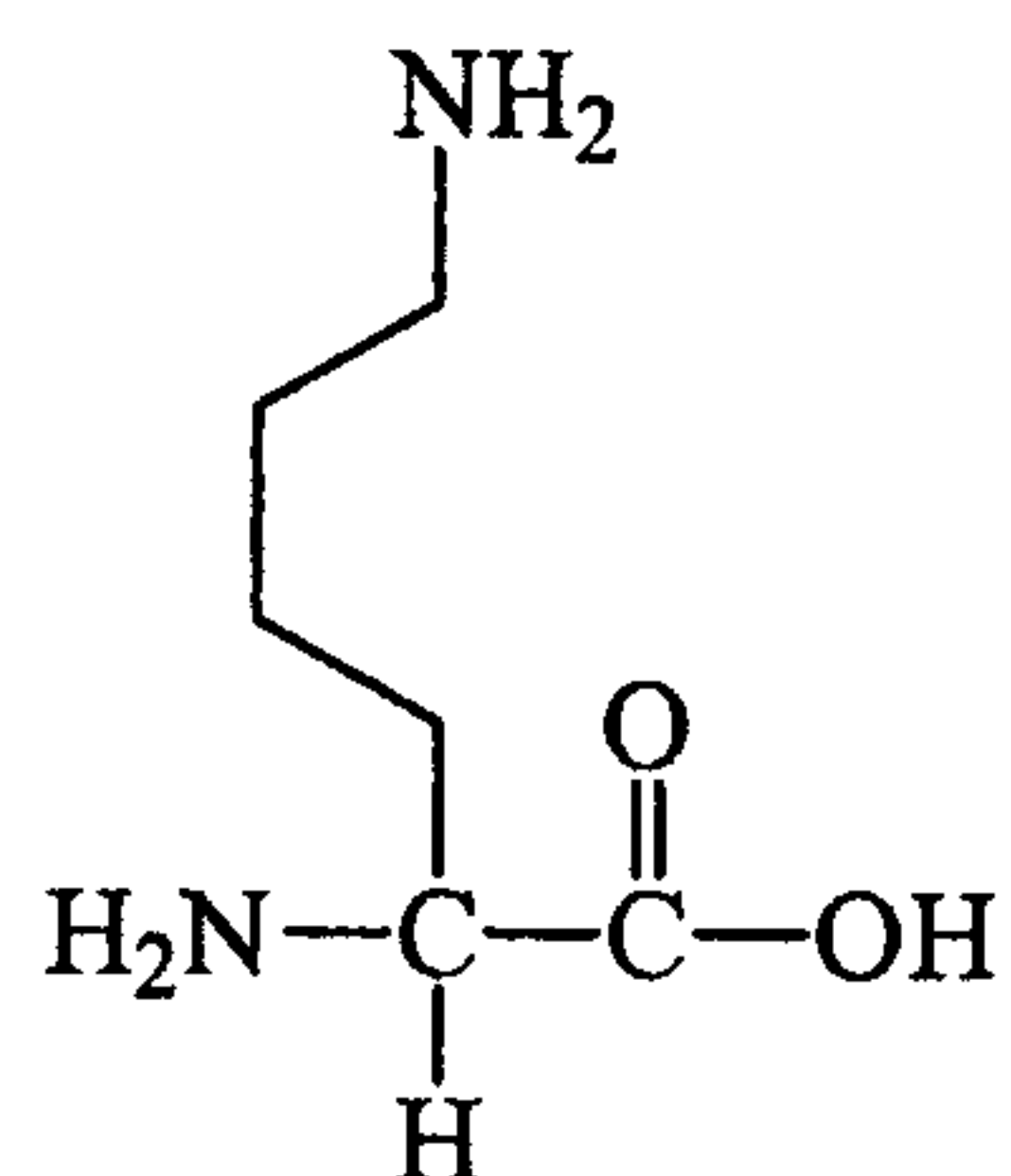
Another preferred suds stabilizing polymer are the proteinaceous suds stabilizers. These can be peptides, polypeptides, amino acid containing copolymers, and mixtures thereof. Any suitable amino acid can be used to form the backbone of the peptides, polypeptides, or amino acid containing copolymers of the present invention provided at least 10% to about 40% of said amino acids which comprise the peptides are capable of being protonated at a pH of from 7 to about 11.5.

In general, the amino acids suitable for use in forming the proteinaceous suds stabilizers of the present invention have from 2 to 22 carbon atoms, said amino acids having the formula:



wherein R and R¹ are each independently hydrogen, C₁-C₆ linear or branched alkyl, C₁-C₆ substituted alkyl, and mixtures thereof. The indices x and y are each independently from 0 to 2.

An example of a more preferred amino acid according to the present invention is the amino acid lysine having the formula:

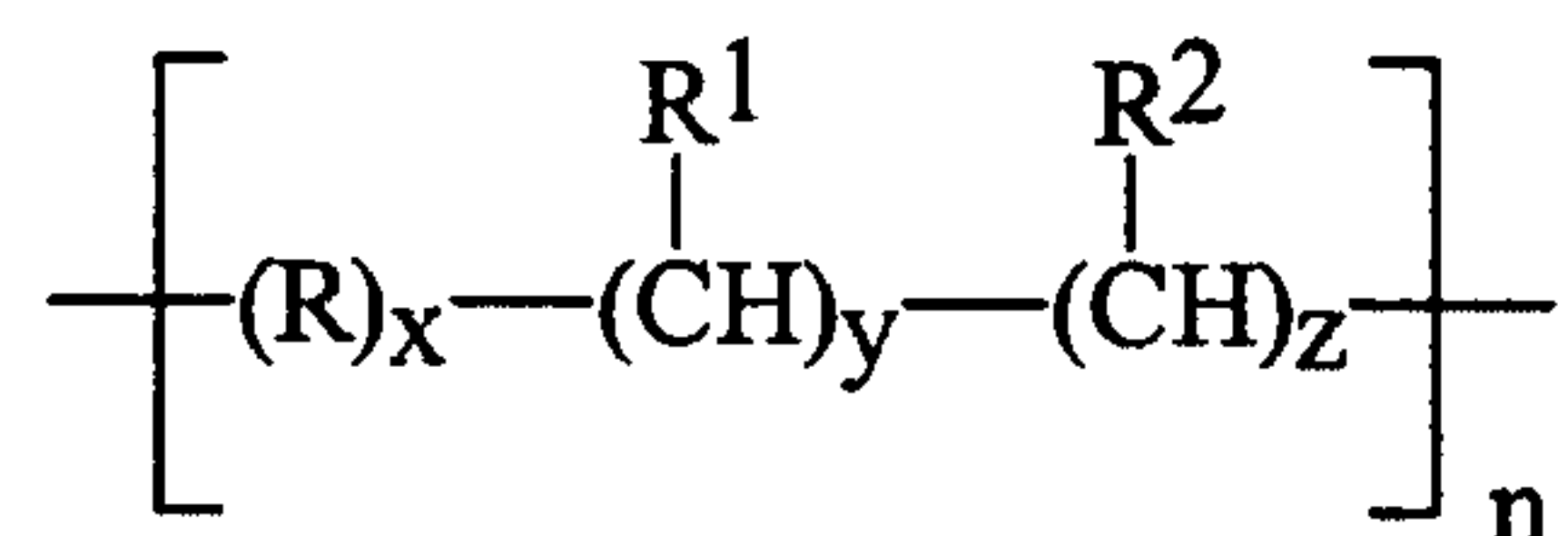


wherein R is a substituted C₁ alkyl moiety, said substituent is 4-imidazolyl.

One type of suitable proteinaceous suds stabilizer is comprised entirely of amino acids. Said polyamino acid compounds may be naturally occurring peptides, polypeptides, enzymes, and the like, provided said compounds have an isoelectric point of from about 7 to about 11.5 and a molecular weight greater than or equal to about 1500 daltons. An example of a polyamino acid which is suitable as a proteinaceous suds stabilizer according to the present invention is the enzyme lysozyme.

Another preferred polymeric suds stabilizers are homopolymers or copolymers wherein the monomers which comprise said homopolymers or copolymers contain a moiety capable of being protonated at a pH of from about 4 to about 12, or a moiety capable of being de-protonated at a pH of from about 4 to about 12, of a mixture of both types of moieties.

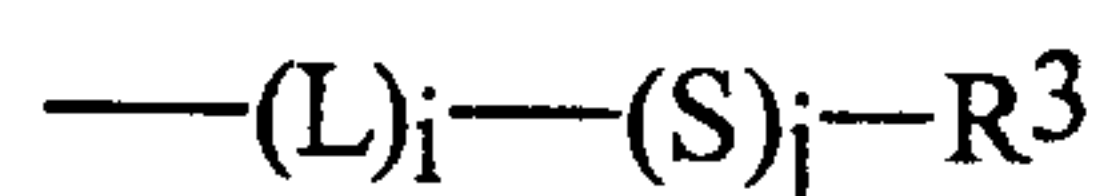
A preferred class of zwitterionic polymer suitable for use as a suds volume and suds duration enhancer has the formula:



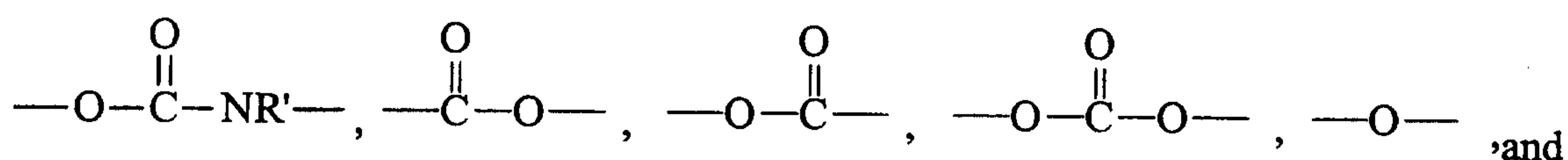
wherein R is C₁-C₁₂ linear alkylene, C₁-C₁₂ branched alkylene, and mixtures thereof; preferably C₁-C₄ linear alkylene, C₃-C₄ branched alkylene; more preferably

methylene and 1,2-propylene. R^1 and R^2 are defined herein after. The index x is from 0 to 6; y is 0 or 1; z is 0 or 1. The index n has the value such that the zwitterionic polymers of the present invention have an average molecular weight of from about 1,000 to about 2,000,000 preferably from about 5,000 to about 1,000,000, more preferably from about 10,000 to about 750,000, more preferably from about 20,000 to about 500,000, even more preferably from about 35,000 to about 300,000 daltons. The molecular weight of the polymeric suds boosters, can be determined via conventional gel permeation chromatography.

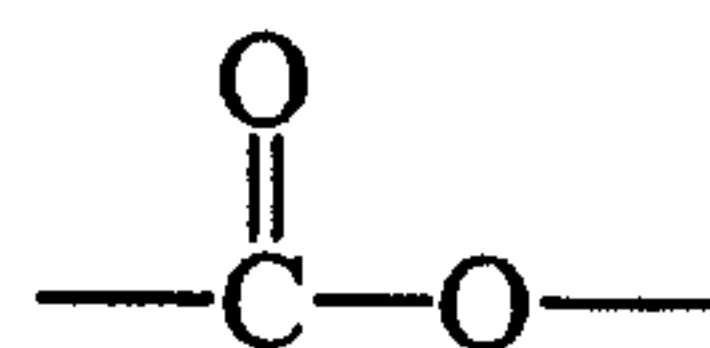
Anionic Units - R^1 is a unit capable of having a negative charge at a pH of from about 4 to about 12. Preferred R^1 has the formula:



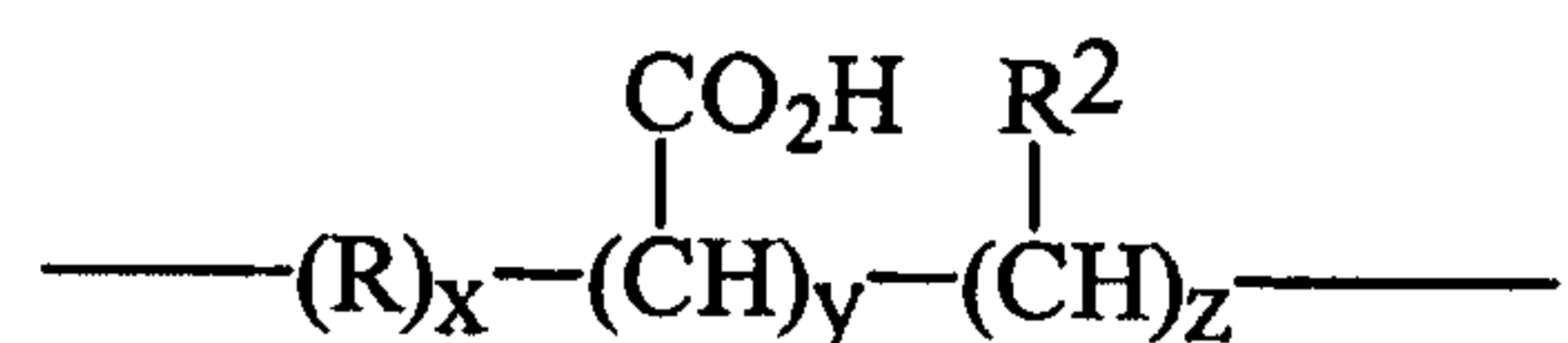
wherein L is a linking unit independently selected from the following:



mixtures thereof, wherein R' is independently hydrogen, C_1 - C_4 alkyl, and mixtures thereof; preferably hydrogen or alternatively R' and S can form a heterocycle of 4 to 7 carbon atoms, optionally containing other hetero atoms and optionally substituted. Preferably the linking group L can be introduced into the molecule as part of the original monomer backbone, for example, a polymer having L units of the formula:



can suitably have this moiety introduced into the polymer via a carboxylate containing monomer, for example, a monomer having the general formula:



When the index i is 0, L is absent.

For anionic units S is a "spacing unit" wherein each S unit is independently selected from C_1 - C_{12} linear alkylene, C_1 - C_{12} branched alkylene, C_3 - C_{12} linear

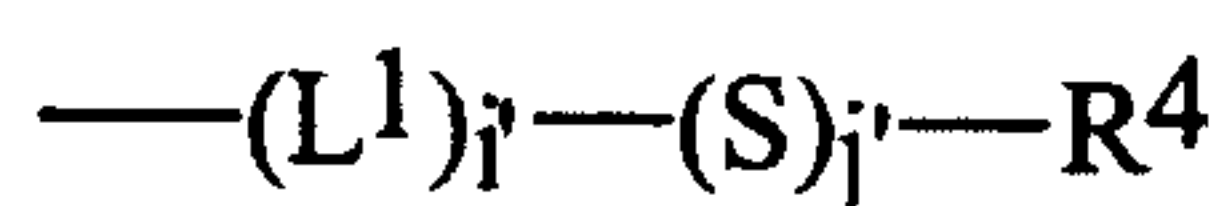
alkenylene, C₃-C₁₂ branched alkenylene, C₃-C₁₂ hydroxyalkylene, C₄-C₁₂ dihydroxyalkylene, C₆-C₁₀ arylene, C₈-C₁₂ dialkylarylene, $-(R^5O)_kR^5-$, $-(R^5O)_kR^6(OR^5)_k-$, $-CH_2CH(OR^7)CH_2-$, and mixtures thereof; wherein R⁵ is C₂-C₄ linear alkylene, C₃-C₄ branched alkylene, and mixtures thereof, preferably ethylene, 1,2-propylene, and mixtures thereof, more preferably ethylene; R⁶ is C₂-C₁₂ linear alkylene, and mixtures thereof, preferably ethylene; R⁷ is hydrogen, C₁-C₄ alkyl, and mixtures thereof, preferably hydrogen. The index k is from 1 to about 20.

R³ is independently selected from hydrogen, -CO₂M, -SO₃M, -OSO₃M, -CH₂P(O)(OM)₂, -OP(O)(OM)₂, units having the formula:

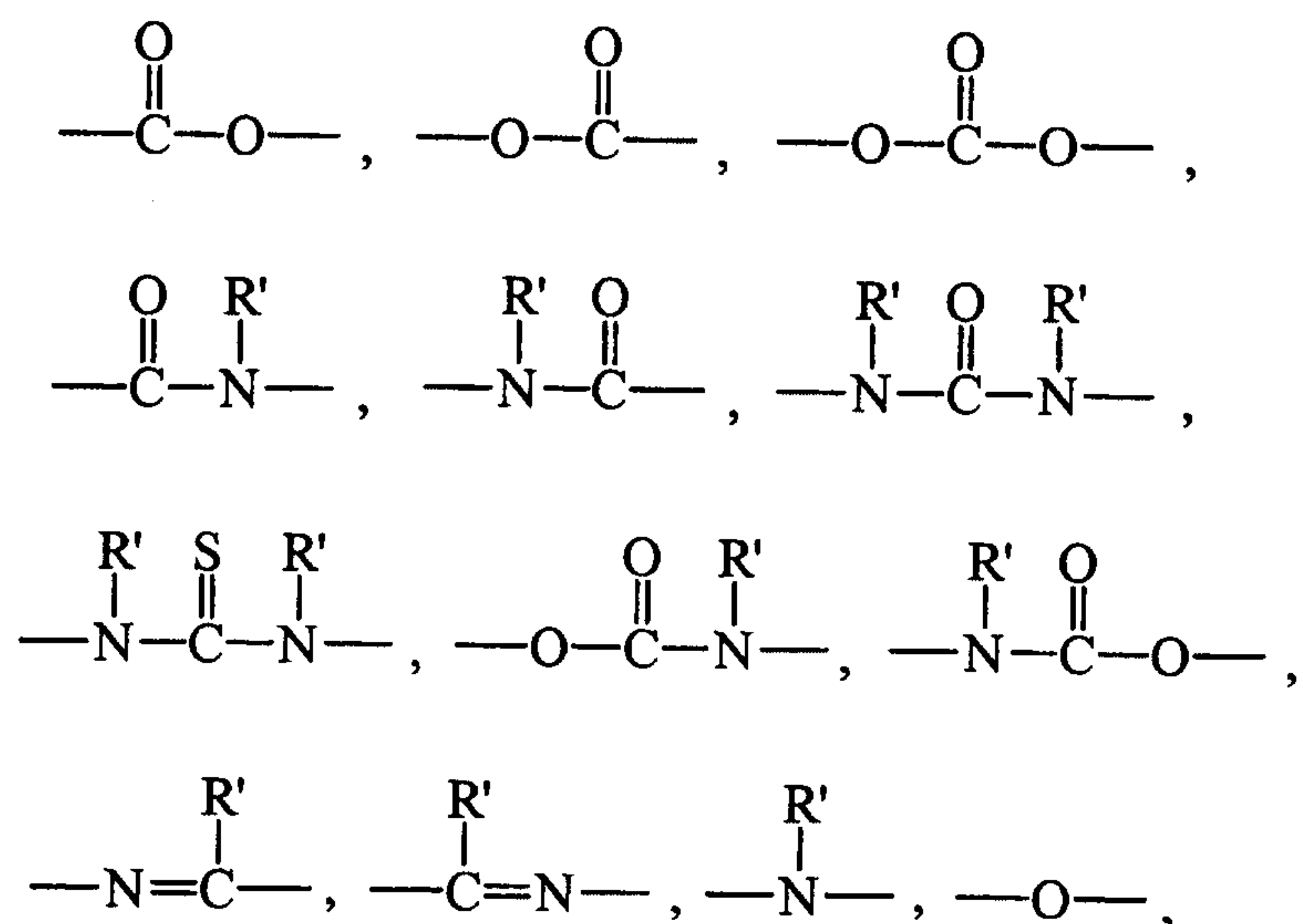


wherein each R⁸, R⁹, and R¹⁰ is independently selected from the group consisting of hydrogen, $-(CH_2)_mR^{11}$, and mixtures thereof, wherein R¹¹ is -CO₂H, -SO₃M, -OSO₃M, -CH(CO₂H)CH₂CO₂H, -CH₂P(O)(OH)₂, -OP(O)(OH)₂, and mixtures thereof, preferably -CO₂H, -CH(CO₂H)CH₂CO₂H, and mixtures thereof, more preferably -CO₂H; provided that one R⁸, R⁹, or R¹⁰ is not a hydrogen atom, preferably two R⁸, R⁹, or R¹⁰ units are hydrogen. M is hydrogen or a salt forming cation, preferably hydrogen. The index m has the value from 0 to 10.

Cationic Units - R² is a unit capable of having a positive charge at a pH of from about 4 to about 12. Preferred R² has the formula:



wherein L¹ is a linking unit independently selected from the following:



and mixtures thereof; wherein R' is independently hydrogen, C₁-C₄ alkyl, and mixtures thereof; preferably hydrogen or alternatively R' and S can form a heterocycle of 4 to 7 carbon atoms, optionally containing other hetero atoms and optionally substituted.

When the index i' is equal to 0, L¹ is absent.

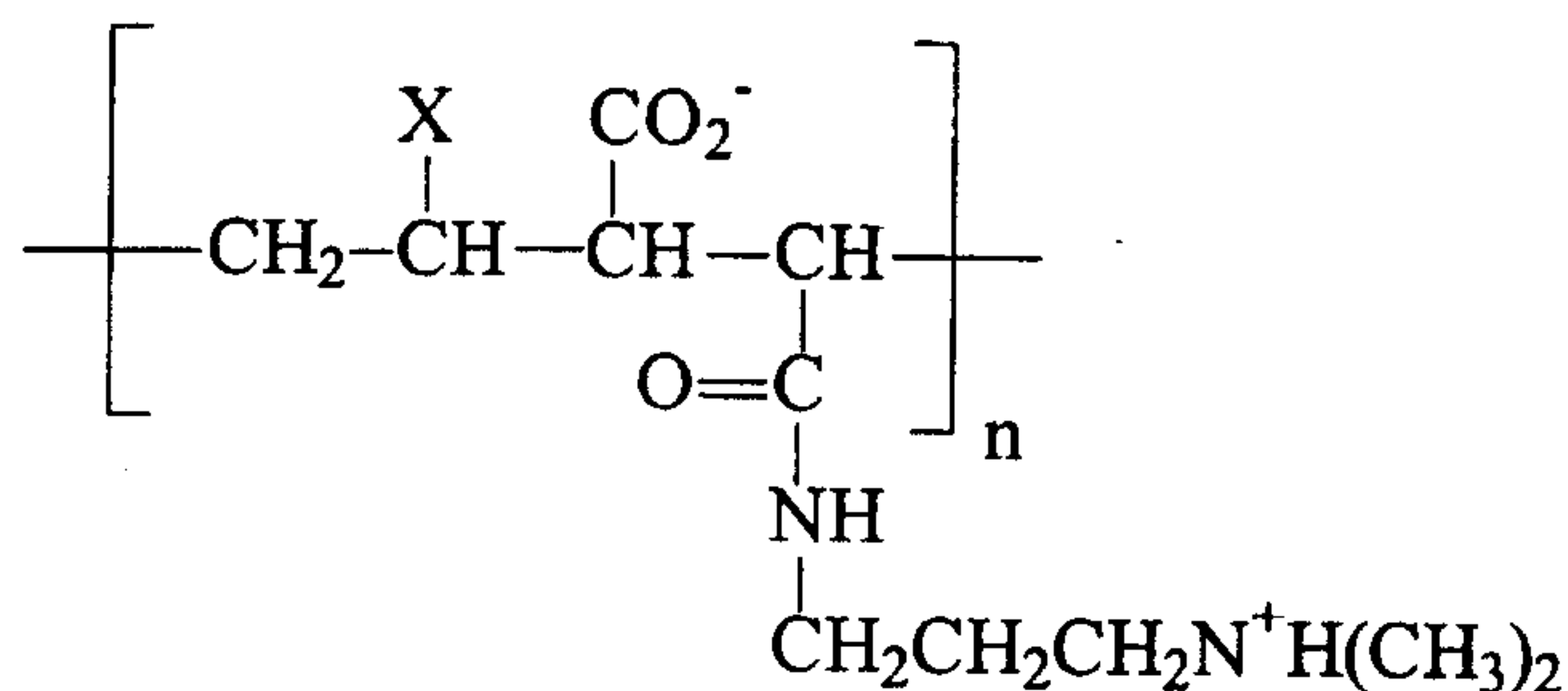
For cationic units S is a "spacing unit" wherein each S unit is independently selected from C₁-C₁₂ linear alkylene, C₁-C₁₂ branched alkylene, C₃-C₁₂ linear alkenylene, C₃-C₁₂ branched alkenylene, C₃-C₁₂ hydroxyalkylene, C₄-C₁₂ dihydroxyalkylene, C₆-C₁₀ arylene, C₈-C₁₂ dialkylarylene, -(R⁵O)_kR⁵-, -(R⁵O)_kR⁶(OR⁵)_k-, -CH₂CH(OR⁷)CH₂-, and mixtures thereof; wherein R⁵ is C₂-C₄ linear alkylene, C₃-C₄ branched alkylene, and mixtures thereof, preferably ethylene, 1,2-propylene, and mixtures thereof, more preferably ethylene; R⁶ is C₂-C₁₂ linear alkylene, and mixtures thereof, preferably ethylene; R⁷ is hydrogen, C₁-C₄ alkyl, and mixtures thereof, preferably hydrogen. The index k is from 1 to about 20.

R⁴ is independently selected from amino, alkylamino carboxamide, 3-imidazolyl, 4-imidazolyl, 2-imidazolyl, 4-imidazolyl, 2-piperidinyl, 3-piperidinyl, 4-piperidinyl, 1-pyrazolyl, 3-pyrazolyl, 4-pyrazolyl, 5-pyrazolyl, 1-pyrazolyl, 3-pyrazolyl, 4-pyrazolyl, 5-pyrazolyl, 2-pyridinyl, 3-pyridinyl, 4-pyridinyl, piperazinyl, 2-pyrrolidinyl, 3-pyrrolidinyl, guanidino, amidino, and mixtures thereof, preferably dialkylamino having the formula:



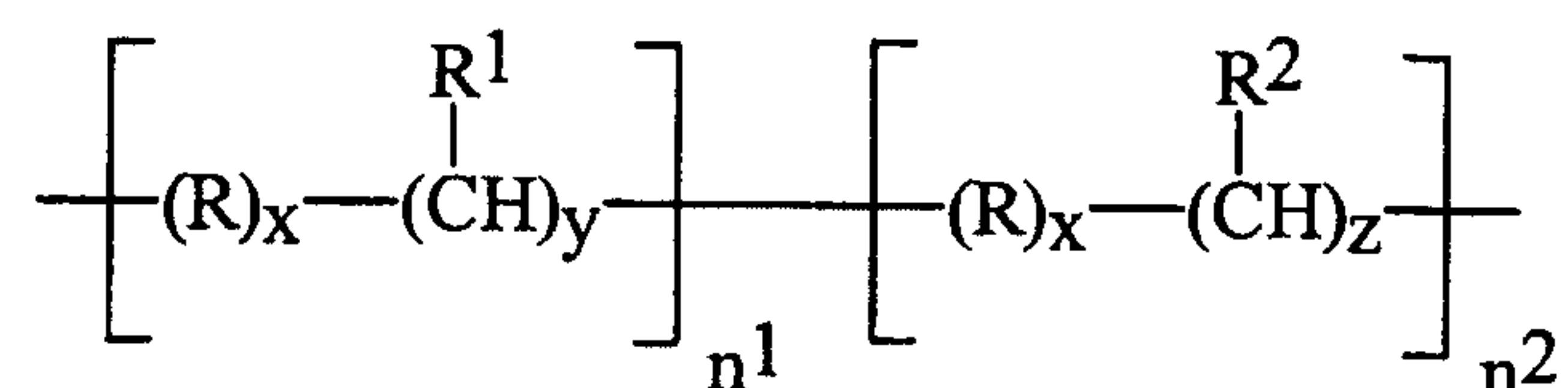
wherein each R^{11} is independently hydrogen, C_1 - C_4 alkyl, and mixtures thereof, preferably hydrogen or methyl or alternatively the two R^{11} can form a heterocycle of 4 to 8 carbon atoms, optionally containing other hetero atoms and optionally substituted.

An example of a preferred zwitterionic polymer according to the present invention has the formula:



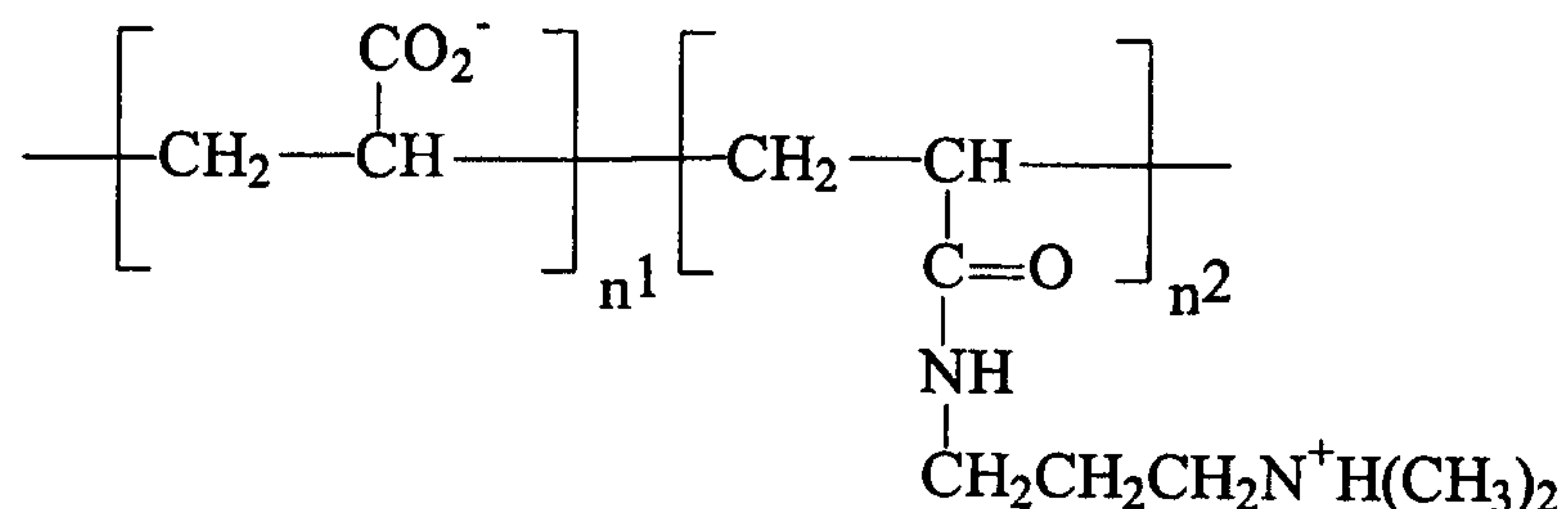
wherein X is C_6 , n has a value such that the average molecular weight is from about 5,000 to about 1,000,000 daltons.

Further preferred zwitterionic polymers according to the present invention are polymers comprising monomers wherein each monomer has only cationic units or anionic units, said polymers have the formula:

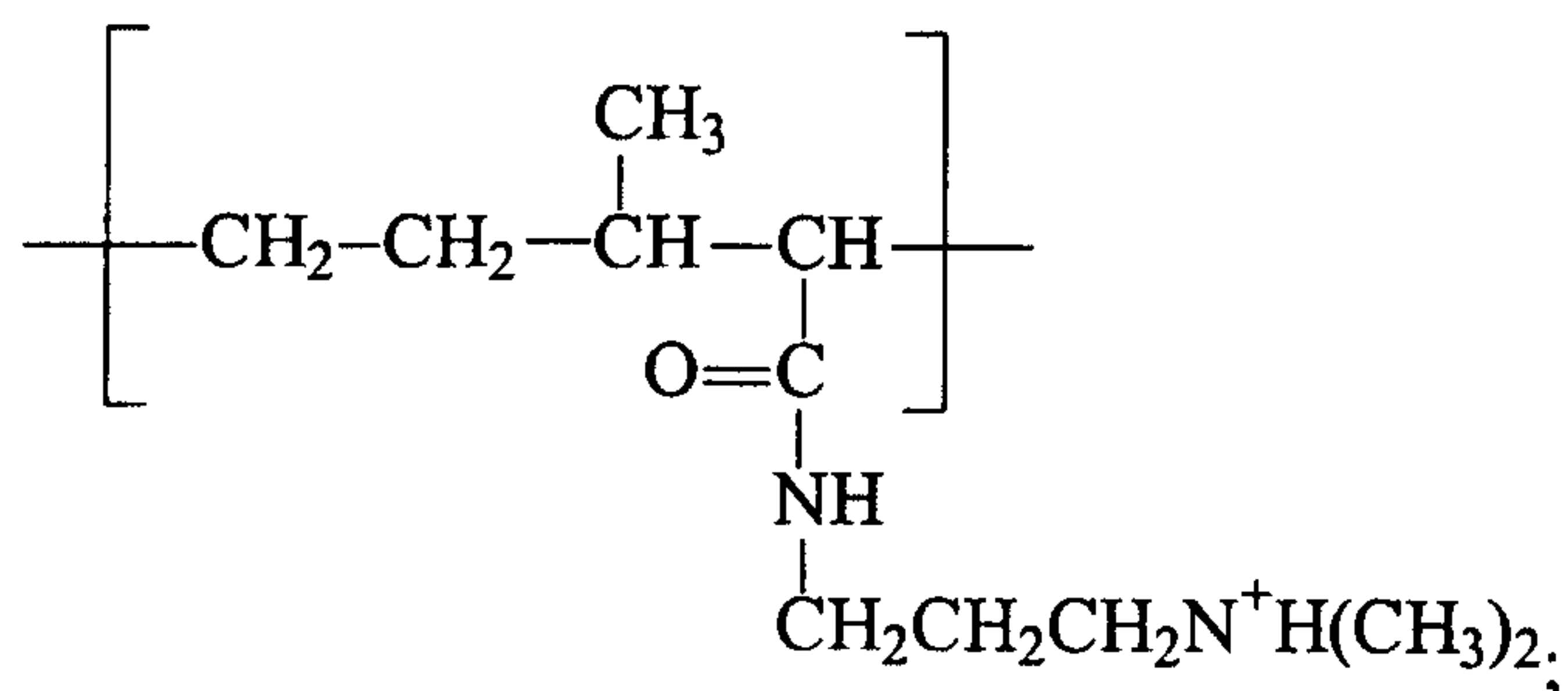


wherein R, R^1 , x, y, and z are the same as defined herein above; $n^1 + n^2 = n$ such that n has a value wherein the resulting zwitterionic polymer has a molecular weight of form about 5,000 to about 1,000,000 daltons.

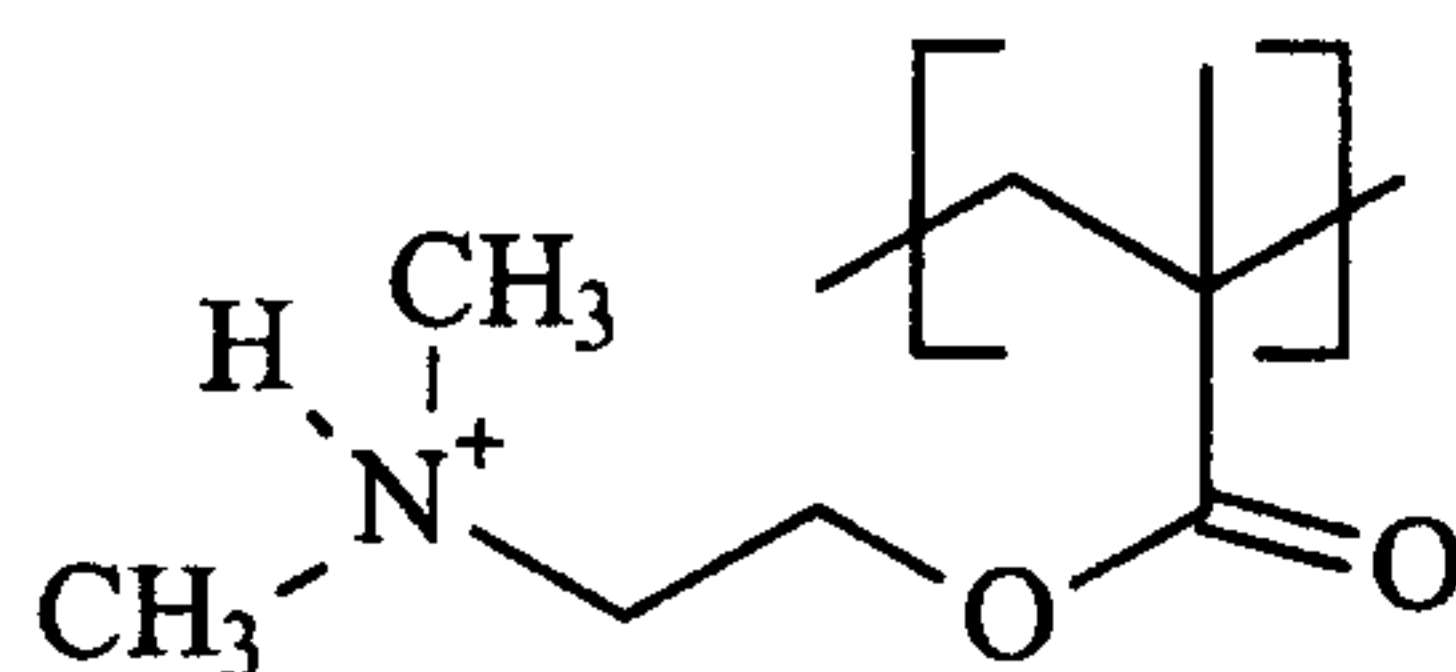
An example of a polymer having monomers with only an anionic unit or a cationic unit has the formula:



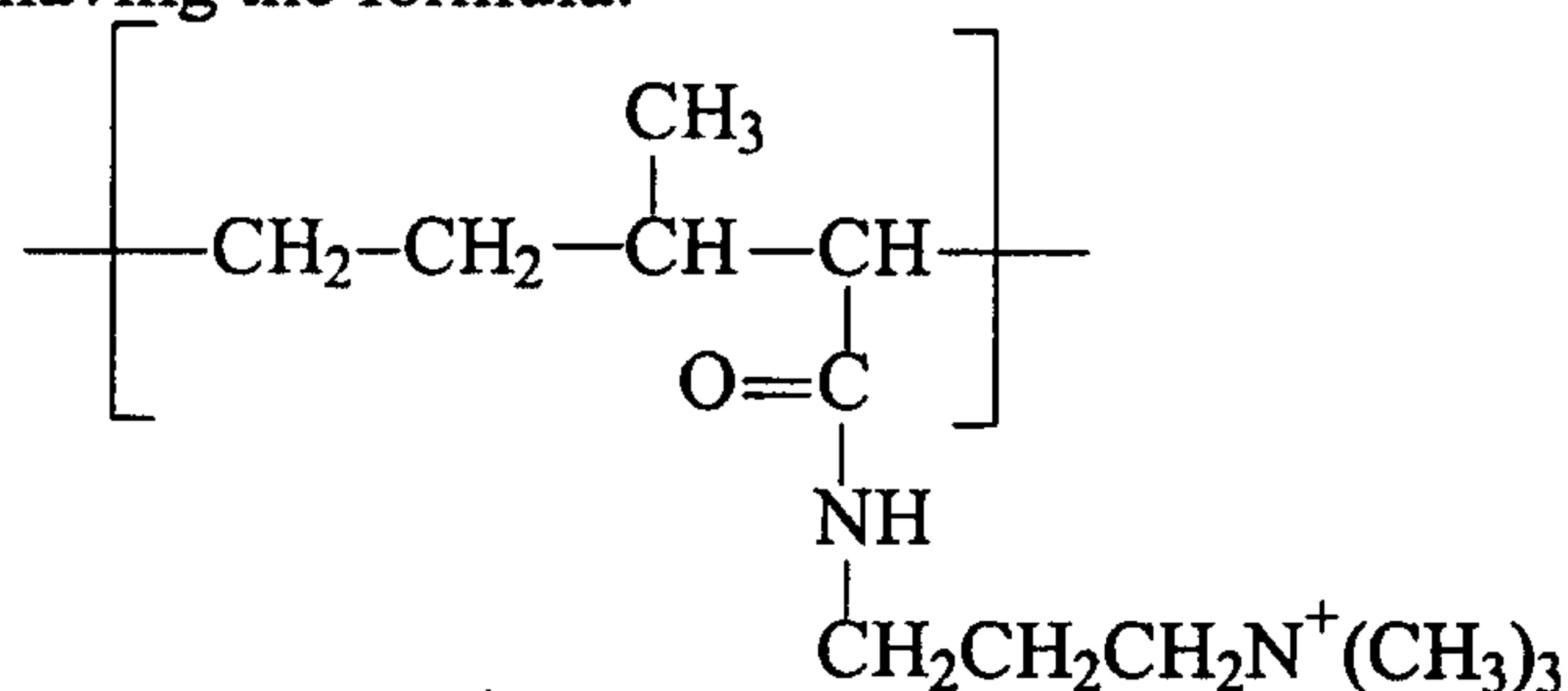
For the purposes of the present invention the term "cationic unit" is defined as "a moiety which when incorporated into the structure of the suds stabilizers of the present invention, is capable of maintaining a cationic charge within the pH range of from about 4 to about 12. The cationic unit is not required to be protonated at every pH value within the range of about 4 to about 12." Non-limiting examples of units which comprise a cationic moiety include lysine, ornithine, the monomeric unit having the formula:



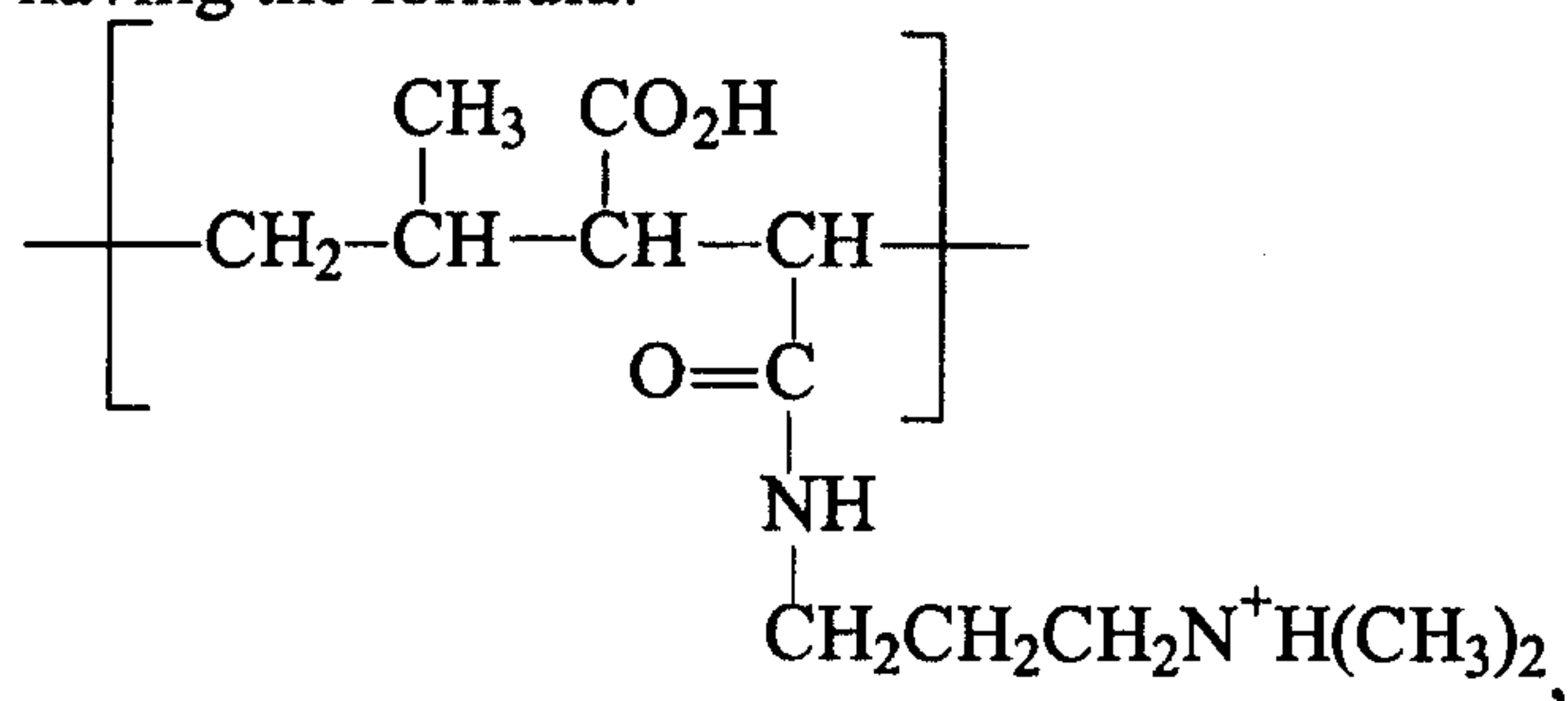
the monomeric unit having the formula:



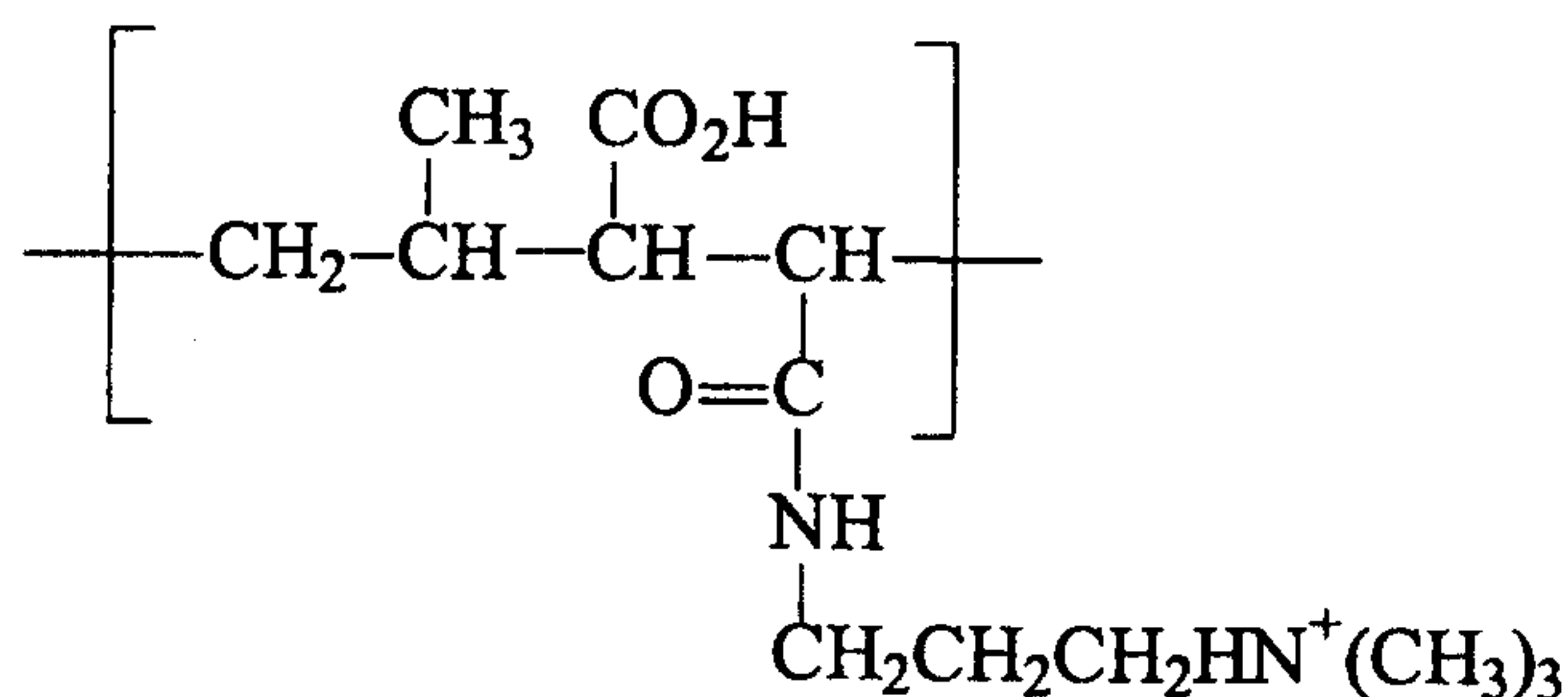
the monomeric unit having the formula:



the monomeric unit having the formula:

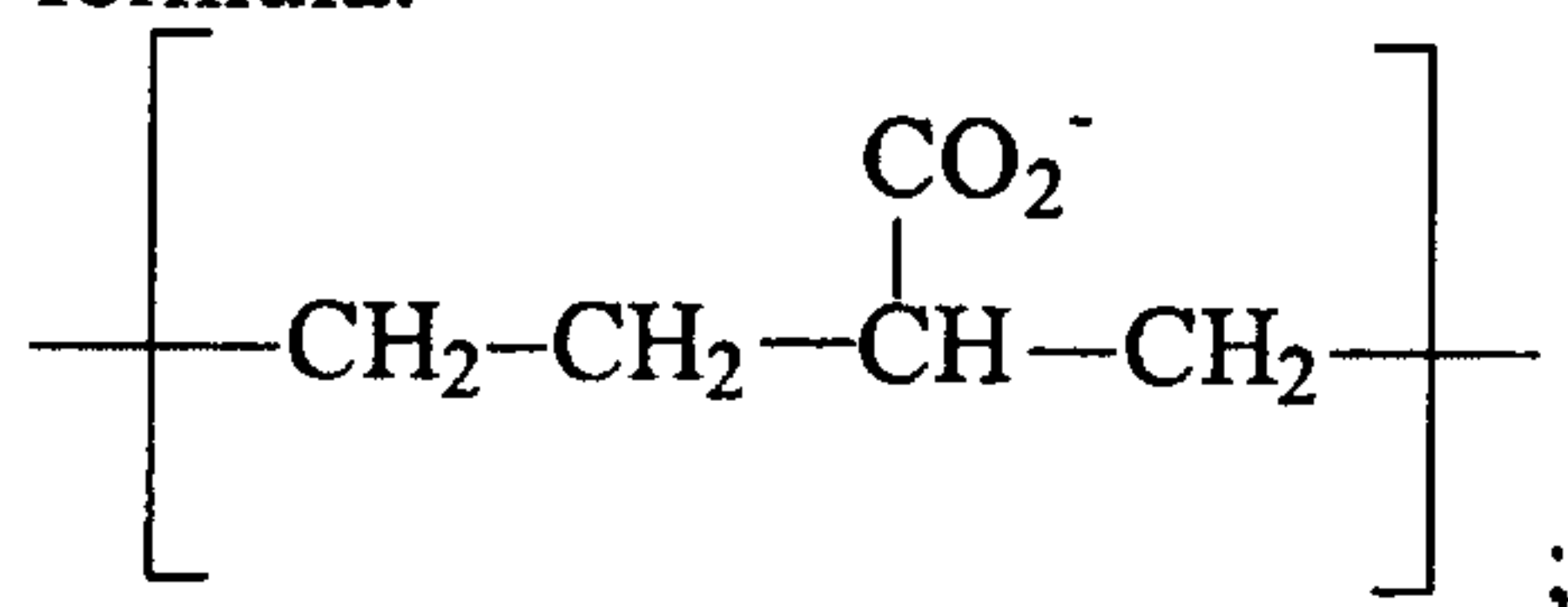


and the monomeric unit having the formula:

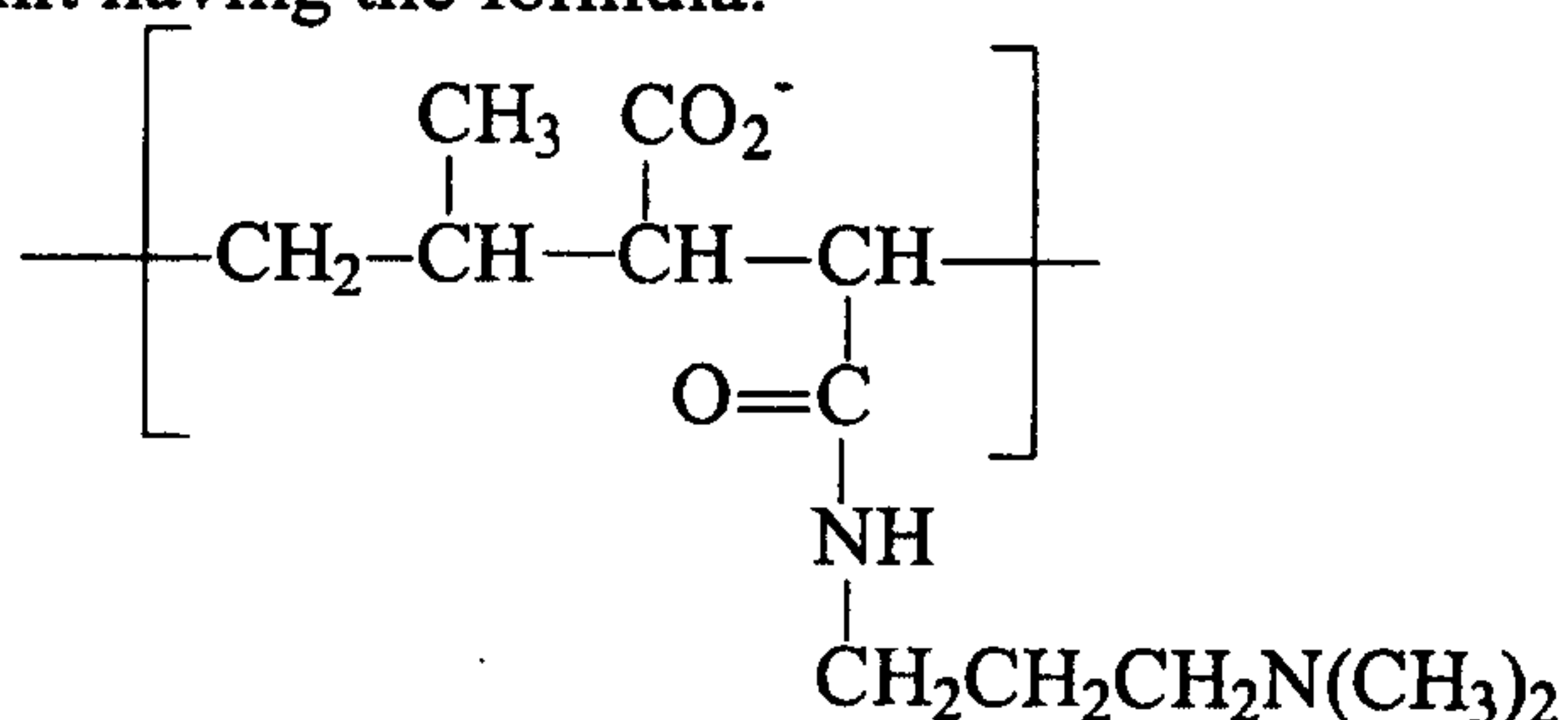


the latter of which also comprises a moiety capable of having an anionic charge at a pH of about 4 to about 12.

For the purposes of the present invention the term "anionic unit" is defined as "a moiety which when incorporated into the structure of the suds stabilizers of the present invention, is capable of maintaining an anionic charge within the pH range of from about 4 to about 12. The anionic unit is not required to be de-protonated at every pH value within the range of about 4 to about 12." Non-limiting examples of units which comprise a anionic moiety include, acrylic acid, methacrylic acid, glutamic acid, aspartic acid, the monomeric unit having the formula:



and the monomeric unit having the formula:



the latter of which also comprises a moiety capable of having a cationic charge at a pH of about 4 to about 12. This latter unit is defined herein as "a unit capable of having an anionic and a cationic charge at a pH of from about 4 to about 12."

For the purposes of the present invention the term "non-charged unit" is defined as "a moiety which when incorporated into the structure of the suds stabilizers of the present invention, has no charge within the pH range of from about 4 to about 12." Non-limiting examples of units which are "non-charged units" are styrene, ethylene, propylene, butylene, 1,2-phenylene, esters, amides, ketones, ethers, and the like.

The units which comprise the polymers of the present invention may, as single units or monomers, have any pK_a value.

The formulator may combine any suitable monomers or units to form a polymeric suds stabilizer, for example, amino acids may be combined with polyacrylate units.

Enzymes other than amylase The compositions of the present invention may further comprise one or more enzymes other than amylase which provide cleaning performance benefits. Said enzymes include enzymes selected from cellulases, hemicellulases, peroxidases, proteases, gluco-amylases, lipases, cutinases, pectinases, xylanases, reductases, oxidases, phenoloxidases, lipoxygenases, ligninases, pullulanases, tannases, pentosanases, malanases, β -glucanases, arabinosidases or mixtures thereof. A preferred combination is a detergent composition having a cocktail of conventional applicable enzymes like protease, amylase, lipase, cutinase and/or cellulase. Enzymes when present in the compositions, at from about 0.0001% to about 5% of active enzyme by weight of the detergent composition.

Proteolytic Enzyme - The proteolytic enzyme can be of animal, vegetable or microorganism (preferred) origin. The proteases for use in the detergent compositions herein include (but are not limited to) trypsin, subtilisin, chymotrypsin and elastase-type proteases. Preferred for use herein are subtilisin-type proteolytic enzymes. Particularly preferred is bacterial serine proteolytic enzyme obtained from Bacillus subtilis and/or Bacillus licheniformis.

Suitable proteolytic enzymes include Novo Industri A/S Alcalase[®] (preferred), Esperase[®], Savinase[®] (Copenhagen, Denmark), Gist-brocades' Maxatase[®], Maxacal[®] and Maxapem 15[®] (protein engineered Maxacal[®]) (Delft, Netherlands), and subtilisin BPN and BPN'(preferred), which are commercially available. Preferred proteolytic enzymes are also modified bacterial serine proteases, such as those made by Genencor International, Inc. (San Francisco, California) which are described in European Patent 251,446B, granted December 28, 1994 (particularly pages 17, 24 and 98) and which are also called herein "Protease B". U.S. Patent 5,030,378, Venegas, issued July 9, 1991,

refers to a modified bacterial serine proteolytic enzyme (Genencor International) which is called "Protease A" herein (same as BPN'). In particular see columns 2 and 3 of U.S. Patent 5,030,378 for a complete description, including amino sequence, of Protease A and its variants. Other proteases are sold under the trade marks: Primase, Durazym, Opticlean and Optimase. Preferred proteolytic enzymes, then, are selected from the group consisting of Alcalase[®] (Novo Industri A/S), BPN', Protease A and Protease B (Genencor), and mixtures thereof. Protease B is most preferred.

Of particular interest for use herein are the proteases described in U.S. Patent No. 5,470,733.

Other proteases can be included in the detergent composition of the invention.

Another preferred protease, referred to as "Protease D" is a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid for a plurality of amino acid residues at a position in said carbonyl hydrolase equivalent to position +76, preferably also in combination with one or more amino acid residue positions equivalent to those selected from the group consisting of +99, +101, +103, +104, +107, +123, +27, +105, +109, +126, +128, +135, +156, +166, +195, +197, +204, +206, +210, +216, +217, +218, +222, +260, +265, and/or +274 according to the numbering of *Bacillus amyloliquefaciens* subtilisin, as described in WO 95/10615 published April 20, 1995 by Genencor International (A. Baeck et al. entitled "Protease-Containing Cleaning Compositions" having U.S. Patent No. 5,679,630).

Useful proteases are also described in PCT publications: WO 95/30010 published November 9, 1995 by The Procter & Gamble Company; WO 95/30011 published November 9, 1995 by The Procter & Gamble Company; WO 95/29979 published November 9, 1995 by The Procter & Gamble Company.

Protease enzyme may be incorporated into the compositions in accordance with the invention at a level of from 0.0001% to 2% active enzyme by weight of the composition.

Various carbohydrase enzymes which impart antimicrobial activity may also be included in the present invention. Such enzymes include endoglycosidase, Type II endoglycosidase and glucosidase as disclosed in U.S. Patent Nos. 5,041,236, 5,395,541,

5,238,843 and 5,356,803.

Of course, other enzymes having antimicrobial activity may be employed as well including peroxidases, oxidases and various other enzymes.

It is also possible to include an enzyme stabilization system into the compositions of the present invention when any enzyme is present in the composition.

Perfumes - Perfumes and perfumery ingredients useful in the present compositions and processes comprise a wide variety of natural and synthetic chemical ingredients, including, but not limited to, aldehydes, ketones, esters, and the like. Also included are various natural extracts and essences which can comprise complex mixtures of ingredients, such as orange oil, lemon oil, rose extract, lavender, musk, patchouli, balsamic essence, sandalwood oil, pine oil, cedar, and the like. Finished perfumes can comprise extremely complex mixtures of such ingredients. Finished perfumes typically comprise from about 0.01% to about 2%, by weight, of the detergent compositions herein, and individual perfumery ingredients can comprise from about 0.0001% to about 90% of a finished perfume composition.

Non-limiting examples of perfume ingredients useful herein include: 7-acetyl-1,2,3,4,5,6,7,8-octahydro-1,1,6,7-tetramethyl naphthalene; ionone methyl; ionone gamma methyl; methyl cedrylone; methyl dihydrojasmonate; methyl 1,6,10-trimethyl-2,5,9-cyclododecatrien-1-yl ketone; 7-acetyl-1,1,3,4,4,6-hexamethyl tetralin; 4-acetyl-6-tert-butyl-1,1-dimethyl indane; para-hydroxy-phenyl-butanone; benzophenone; methyl beta-naphthyl ketone; 6-acetyl-1,1,2,3,3,5-hexamethyl indane; 5-acetyl-3-isopropyl-1,1,2,6-tetramethyl indane; 1-dodecanal, 4-(4-hydroxy-4-methylpentyl)-3-cyclohexene-1-carboxaldehyde; 7-hydroxy-3,7-dimethyl octanal; 10-undecen-1-al; iso-hexenyl cyclohexyl carboxaldehyde; formyl tricyclodecane; condensation products of hydroxycitronellal and methyl anthranilate, condensation products of hydroxycitronellal and indol, condensation products of phenyl acetaldehyde and indol; 2-methyl-3-(para-tert-butylphenyl)-propionaldehyde; ethyl vanillin; heliotropin; hexyl cinnamic aldehyde; amyl cinnamic aldehyde; 2-methyl-2-(para-iso-propylphenyl)-propionaldehyde; coumarin; decalactone gamma; cyclopentadecanolide; 16-hydroxy-9-hexadecenoic acid lactone; 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-gamma-2-benzopyrane; beta-naphthol methyl ether; ambroxane; dodecahydro-3a,6,6,9a-tetramethyl-

naphtho[2,1b]furan; cedrol, 5-(2,2,3-trimethylcyclopent-3-enyl)-3-methylpentan-2-ol; 2-ethyl-4-(2,2,3-trimethyl-3-cyclopenten-1-yl)-2-buten-1-ol; caryophyllene alcohol; tricyclodecenyl propionate; tricyclodecenyl acetate; benzyl salicylate; cedryl acetate; and para-(tert-butyl) cyclohexyl acetate.

Particularly preferred perfume materials are those that provide the largest odor improvements in finished product compositions containing cellulases. These perfumes include but are not limited to: hexyl cinnamic aldehyde; 2-methyl-3-(para-tert-butylphenyl)-propionaldehyde; 7-acetyl-1,2,3,4,5,6,7,8-octahydro-1,1,6,7-tetramethyl naphthalene; benzyl salicylate; 7-acetyl-1,1,3,4,4,6-hexamethyl tetralin; para-tert-butyl cyclohexyl acetate; methyl dihydro jasmonate; beta-naphthol methyl ether; methyl beta-naphthyl ketone; 2-methyl-2-(para-iso-propylphenyl)-propionaldehyde; 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl-cyclopenta-gamma-2-benzopyrane; dodecahydro-3a,6,6,9a-tetramethylnaphtho[2,1b]furan; anisaldehyde; coumarin; cedrol; vanillin; cyclopentadecanolide; tricyclodecenyl acetate; and tricyclodecenyl propionate.

Other perfume materials include essential oils, resinoids, and resins from a variety of sources including, but not limited to: Peru balsam, Olibanum resinoid, styrax, labdanum resin, nutmeg, cassia oil, benzoin resin, coriander and lavandin. Still other perfume chemicals include phenyl ethyl alcohol, terpineol, linalool, linalyl acetate, geraniol, nerol, 2-(1,1-dimethylethyl)-cyclohexanol acetate, benzyl acetate, and eugenol. Carriers such as diethylphthalate can be used in the finished perfume compositions.

Dispersant Polymers

The compositions used in the methods of the present invention may also optionally contain from about 0.1% to about 20%, more preferably from about 0.5% to about 10% by weight of the composition of a dispersant polymer. Dispersant polymers are compounds which act as soil suspending agents in the aqueous wash liquor. That is, they act to suspend the soils in solution and prevent the soils from re-depositing on the surfaces of fabrics or dishes. This allows soils to be removed with the wash liquor. Dispersant polymers are well-known and conventional and are available from BASF Corp. and Rohm & Haas. Typical examples include polyethoxylated amines and acrylic acid/maleic acid copolymers.

Soil Release Agents

The compositions according to the present invention may optionally comprise one or more soil release agents. Polymeric soil release agents are characterized by having both hydrophilic segments, to hydrophilize the surface of hydrophobic fibers, such as polyester and nylon, and hydrophobic segments, to deposit upon hydrophobic fibers and remain adhered thereto through completion of the laundry cycle and , thus, serve as an anchor for the hydrophilic segments. This can enable stains occurring subsequent to treatment with the soil release agent to be more easily cleaned in later washing procedures.

If utilized, soil release agents will generally comprise from about 0.01% to about 10% preferably from about 0.1% to about 5%, more preferably from about 0.2% to about 3% by weight, of the composition.

The following describe soil release polymers suitable for use in the present invention. U.S. 5,691,298 Gosselink et al., issued November 25, 1997; U.S. 5,599,782 Pan et al., issued February 4, 1997; U.S. 5,415,807 Gosselink et al., issued May 16, 1995; U.S. 5,182,043 Morrall et al., issued January 26, 1993; U.S. 4,956,447 Gosselink et al., issued September 11, 1990; U.S. 4,976,879 Maldonado et al. issued December 11, 1990; U.S. 4,968,451 Scheibel et al., issued November 6, 1990; U.S. 4,925,577 Borchert, Sr. et al., issued May 15, 1990; U.S. 4,861,512 Gosselink, issued August 29, 1989; U.S. 4,877,896 Maldonado et al., issued October 31, 1989; U.S. 4,771,730 Gosselink et al., issued October 27, 1987; U.S. 4,711,730 Gosselink et al., issued December 8, 1987; U.S. 4,721,580 Gosselink issued January 26, 1988; U.S. 4,000,093 Nicol et al., issued December 28, 1976; U.S. 3,959,230 Hayes, issued May 25, 1976; U.S. 3,893,929 Basadur, issued July 8, 1975; and European Patent Application 0 219 048, published April 22, 1987 by Kud et al.

Further suitable soil release agents are described in U.S. 4,201,824 Voilland et al.; U.S. 4,240,918 Lagasse et al.; U.S. 4,525,524 Tung et al.; U.S. 4,579,681 Ruppert et al.; U.S. 4,220,918; U.S. 4,787,989; EP 279,134 A, 1988 to Rhone-Poulenc Chemie; EP 457,205 A to BASF (1991); and DE 2,335,044 to Unilever N.V., 1974.

Brightener

Any optical brighteners or other brightening or whitening agents known in the art can be present at levels typically from about 0.05% to about 1.2%, by weight, in the compositions used herein. Commercial optical brighteners which may be useful in the present invention can be classified into subgroups, which include, but are not necessarily limited to, derivatives of stilbene, pyrazoline, coumarin, carboxylic acid, methinecyanines, dibenzothiophene-5,5-dioxide, azoles, 5- and 6-membered-ring heterocycles, and other miscellaneous agents. Examples of such brighteners are disclosed in "The Production and Application of Fluorescent Brightening Agents", M. Zahradnik, Published by John Wiley & Sons, New York (1982).

Specific examples of optical brighteners which are useful in the present compositions are those identified in U.S. Patent 4,790,856, issued to Wixon on December 13, 1988. These brighteners include the PHORWHITE™ series of brighteners from Verona. Other brighteners disclosed in this reference include: Tinopal™ UNPA, Tinopal CBS and Tinopal 5BM; available from Ciba-Geigy; Artic White™ CC and Artic White CWD, available from Hilton-Davis, located in Italy; the 2-(4-styryl-phenyl)-2H-naphthol[1,2-d]triazoles; 4,4'-bis-(1,2,3-triazol-2-yl)-stilbenes; 4,4'-bis(styryl)bisphenyls; and the aminocoumarins. Specific examples of these brighteners include 4-methyl-7-diethyl-amino coumarin; 1,2-bis(-benzimidazol-2-yl)ethylene; 1,3-diphenyl-phrazolines; 2,5-bis(benzoxazol-2-yl)thiophene; 2-styryl-naphth-[1,2-d]oxazole; and 2-(stilbene-4-yl)-2H-naphtho-[1,2-d]triazole. See also U.S. Patent 3,646,015, issued February 29, 1972 to Hamilton. Anionic brighteners are preferred herein.

Other Ingredients - The compositions can further preferably comprise one or more deterative adjuncts selected from the following: polysaccharides, abrasives, bactericides, tarnish inhibitors, dyes, buffers, antifungal or mildew control agents, insect repellents, perfumes, thickeners, processing aids, anti-corrosive aids, stabilizers and antioxidants. A wide variety of other ingredients useful in detergent compositions can be included in the compositions herein, including other active ingredients, carriers, antioxidants, processing aids, dyes or pigments, solvents for liquid formulations, etc.

Usual ingredients can include one or more materials for assisting or enhancing cleaning performance, treatment of the substrate to be cleaned, or to modify the aesthetics of the composition. Usual deterative adjuncts of detergent compositions

include the ingredients set forth in U.S. Pat. No. 3,936,537, Baskerville et al. Adjuncts which can also be used in the compositions employed in the present invention, in their conventional art-established levels for use (generally from 0% to about 20% of the detergent ingredients, preferably from about 0.5% to about 10%), include other active ingredients such as enzyme stabilizers, color speckles, anti-tarnish and/or anti-corrosion agents, dyes, fillers, optical brighteners, germicides, alkalinity sources, anti-oxidants, enzyme stabilizing agents, perfumes, dyes, solubilizing agents, clay soil removal/anti-redeposition agents, carriers, processing aids, pigments, solvents for liquid formulations, fabric softeners, static control agents, etc. Dye transfer inhibiting agents, including polyamine N-oxides such as polyvinylpyridine N-oxide can be used. Dye-transfer-inhibiting agents are further illustrated by polyvinylpyrrolidone and copolymers of N-vinyl imidazole and N-vinyl pyrrolidone. If desired, soluble magnesium salts such as $MgCl_2$, $MgSO_4$, and the like, can be added at levels of, typically, 0.1%-2%, to enhance grease removal performance.

Various deterative ingredients employed in the present compositions optionally can be further stabilized by absorbing said ingredients onto a porous hydrophobic substrate, then coating said substrate with a hydrophobic coating. Preferably, the deterative ingredient is admixed with a surfactant before being absorbed into the porous substrate. In use, the deterative ingredient is released from the substrate into the aqueous washing liquor, where it performs its intended deterative function.

To illustrate this technique in more detail, a porous hydrophobic silica (trademark SIPERNAT D10, DeGussa) is admixed with a proteolytic enzyme solution containing 3%-5% of C_{13-15} ethoxylated alcohol (EO 7) nonionic surfactant. Typically, the enzyme/surfactant solution is 2.5 X the weight of silica. The resulting powder is dispersed with stirring in silicone oil (various silicone oil viscosities in the range of 500-12,500 can be used). The resulting silicone oil dispersion is emulsified or otherwise added to the final detergent matrix. By this means, ingredients such as the aforementioned enzymes, bleaches, bleach activators, bleach catalysts, photoactivators, dyes, fluorescers, fabric conditioners and hydrolyzable surfactants can be "protected" for use in detergent compositions.

An antioxidant can be optionally added to the detergent compositions of the present invention. They can be any conventional antioxidant used in detergent compositions, such as 2,6-di-tert-butyl-4-methylphenol (BHT), carbamate, ascorbate, thiosulfate, monoethanolamine(MEA), diethanolamine, triethanolamine, etc. It is preferred that the antioxidant, when present, be present in the composition from about 0.001% to about 5% by weight.

The compositions of this invention can be in any form, including liquid, tablet, paste, gel, microemulsion or tricritical composition. Highly preferred embodiments are in liquid or gel form. Liquid detergent compositions can contain water and other solvents as carriers. Low molecular weight primary or secondary alcohols exemplified by methanol, ethanol, propanol, and isopropanol are suitable. Monohydric alcohols are preferred for solubilizing surfactant, but polyols such as those containing from 2 to about 6 carbon atoms and from 2 to about 6 hydroxy groups (e.g., 1,3-propanediol, ethylene glycol, glycerine, and 1,2-propanediol) can also be used. The compositions may contain from 5% to 90%, typically 10% to 50% of such carriers.

An example of the procedure for making liquid compositions herein is as follows:

- To the free water and citrate are added and dissolved. To this solution amine oxide, betaine, ethanol, hydrotrope and nonionic surfactant are added. If free water isn't available, the citrate are added to the above mix then stirred until dissolved. At this point, an acid is added to neutralize the formulation. It is preferred that the acid be chosen from organic acids such as maleic and citric, however, inorganic mineral acids may be employed as well. In preferred embodiments these acids are added to the formulation followed by diamine addition. AExS is added last.

Compositions of the invention will have a pH range of from about 2 to about 13, preferably, pH is alkaline, more preferably from about 7 to about 12.5, more preferably from about 8 to about 12, even more preferably from about 9 to about 11.5.

Examples

The following Examples further illustrate the present invention, but are not intended to be limiting thereof.

Ultrasonic energy greatly enhanced starch soil removal and is synergetic with the use of amylase.

Treatment	% Starch Removal (46°C, 7 gpg)	
	5 min ultrasonic soak	5 min. soak
3% pc	Ultrasonic Bath	Soak + ADW Rinse
Composition 1(see below)	42	2
Composition 1 + amylase enzyme* (1.5 ppm TTW)	98	44

- (i) ADW rinse: European miniwasher, short (5 min.) ramp up to 44°C, 7gpg
- (ii) Ultrasonic Bath (no presoak): 2 starch coupons suspended in the middle of a Branson 2210 Sonic cleaner
- (iii) 1.5 ppm TTW corresponds to 0.005% amylase in product
- (iv) The ultrasonic energy used here is ~50-70 watts.

Ultrasonics enhances the performance of bleach catalyst bleaching system on tea stain under short soak times. The addition of ultrasonics provides minimal cleaning benefits to tea stain removal using LDL3.

<u>Treatments</u>	Tea Stained Mug Grade (scale 1-10; worst-best)			
	<u>2 minutes</u>		<u>5 minutes</u>	
	soak	ultrasonic soak	soak	ultrasonic soak
LDL3, 3% pc	2	4.8	3	5
ADW composition (3000 ppm TTW)	5	9	7.5	n/a

- (i) Soak conditions: 46C, 400 rpm, 7gpg, 250 ml volume
- (ii) Ultrasonic soak conditions: 46C, 7gpg, Branson ultrasonic bath Model 2210, 250 ml volume
- (iii) Contains 0.004%Acetatopentaamine cobalt (0.24 ppm TTW in this test)

Direct contact of transducer to soil is the approach being used for the design of the hand held implement.

Treatments	% Egg soil removal (0.4% product concentration 2S)
Soak + ADW Rinse	22
Coupon suspended in middle of the bath	45
Coupon in contact with transducer	66

¹ Branson 2210 Ultrasonic cleaner, 46°C, 7gpg

PASTA SOIL REMOVAL

Significant cleaning occurs with the ultrasonic implement after 7 controlled strokes on pasta soil. The weight of the implement nil ultrasonic energy removes more soil than a Scotch-Brite™ pad alone.

<u>Conditions (composition 1 + 0.005% Amylase, ~40C)</u>	% Pasta Soil Removal
7 strokes with a Scotch-Brite pad (nil ultrasound)	30
7 strokes with ultrasonic implement (+ ultrasound)	86
7 strokes with ultrasonic implement (- ultrasound)	48

Each condition was an average of 2 coupons

Composition of uses in this test

	Composition 1	Composition 2
10% pH	7.8	10.0
AE0.6S	26.28	29.0
Amine oxide	1.73	7.5
ADM Betaine	1.73	---
C11E9	---	4.88
C10E8	4.56	---
NN, dialkyl glucamine	1.37	---
Diamine	---	4.88
Mg++	0.46	---

ADW composition	%
Phosphate	25.47
Carbonate	30.50
Sulfate	20.19
Silicate	5.69
Nonionic surfactant	1.84
Perborate	4.34
protease enzyme	0.90
PAAN	0.004
Water, perfume, minors etc.,	qs to 100%

What is claimed is:

1. An ultrasonic cleaning product comprising:

(a) a cleaning composition comprising an ultrasonically enhanced cleaning agent which is a bleach catalyst; and

(b) a sonic or ultrasonic wave generating source for imparting sonic or ultrasonic waves, said sonic or ultrasonic wave generating source including a transducer wherein said transducer oscillates at a frequency of from about 100 Hz to about 20,000 Hz.

2. The ultrasonic cleaning product of claim 1 wherein the ultrasonically enhanced cleaning agent is present in the cleaning composition from 0.0001% to 40% by weight.

3. The ultrasonic cleaning product according to claim 1 or 2 wherein the bleach catalyst is selected from the group consisting of manganese bleach catalysts, cobalt bleach catalysts, iron bleach catalysts and mixtures thereof.

4. The ultrasonic cleaning product according to any one of claims 1 to 3 wherein said cleaning composition further comprises a conventional cleaning adjunct, said adjunct is selected from the group consisting of builders, surfactants, enzymes other than amylase, bleach activators, bleach boosters, bleaches, alkalinity sources, colorants, perfume, antibacterial agent, lime soap dispersants, polymeric dye transfer inhibiting agents, crystal growth inhibitors, photobleaches, heavy metal ion sequestrants, anti-tarnishing agents, anti-microbial agents, anti-oxidants, anti-redeposition agents, soil release polymers, electrolytes, pH modifiers, thickeners, abrasives, metal ion salts, enzyme stabilizers, corrosion inhibitors, diamines, suds stabilizing polymers, solvents, process aids, fabric softening agents, optical brighteners, hydrotropes and mixtures thereof.

5. The ultrasonic cleaning product according to any one of claims 1 to 4 wherein said sonic or ultrasonic source is a hand-held vibrational ultrasonic device with a cleaning head at the distal end of said device.
6. The ultrasonic cleaning product according to any one of claims 1 to 5 wherein said cleaning composition and said sonic or ultrasonic source are contained together in a device that permits controlled dispensing of said cleaning composition to a hard surface in need of cleaning, while concurrently imparting sonic or ultrasonic waves thereto.
7. The ultrasonic cleaning product according to any one of claims 1 to 6 further comprising instructions for using said product comprising the steps of:
 - (i) applying an effective amount of said cleaning composition to a hard surface; and
 - (ii) imparting sonic or ultrasonic waves to said hard surface using said sonic or ultrasonic source.
8. The ultrasonic cleaning product according to any one of claims 1 to 7 further comprising instructions for using said product comprising the steps of:
 - (i) using said device to apply an effective amount of said cleaning composition to said hard surface concurrently with sonic or ultrasonic waves from said sonic or ultrasonic source; and
 - (ii) moving said sonic or ultrasonic source over and maintain contact thereto said hard surface.
9. A method for removing tough food from a hard surface comprising the steps of:
 - (a) applying an effective amount of a cleaning composition to said tough food on said hard surface, said cleaning composition comprises an

ultrasonically enhanced cleaning agent which is a bleach catalyst; and

(b) imparting sonic or ultrasonic waves to said tough food so as to remove said tough food from said hard surface.

10. The method of claim 9 wherein said sonic or ultrasonic source is a hand-held vibrational ultrasonic device with a cleaning head at the distal end of said device.
11. The method according to any one of claims 9 to 10 wherein said steps (a) and (b) are conducted simultaneously using a device that permits controlled dispensing of said cleaning composition to the stain while concurrently imparting sonic or ultrasonic waves thereto.
12. The method according to any one of claims 9 to 11 wherein said cleaning composition further comprises a conventional cleaning adjunct, said adjunct is selected from the group consisting of builders, surfactants, enzymes, bleach activators, antibacterial agent, bleach catalysts, bleach boosters, bleaches, alkalinity sources, colorants, perfume, lime soap dispersants, polymeric dye transfer inhibiting agents, crystal growth inhibitors, photobleaches, heavy metal ion sequestrants, anti-tarnishing agents, anti-microbial agents, anti-oxidants, anti-redeposition agents, soil release polymers, electrolytes, pH modifiers, thickeners, abrasives, metal ion salts, enzyme stabilizers, corrosion inhibitors, diamines, suds stabilizing polymers, solvents, process aids, fabric softening agents, optical brighteners, hydrotropes and mixtures thereof.
13. The method according to any one of claims 9 to 12 wherein said method comprises the further step of:
 - (c) rinsing said hard surface with an aqueous solution.

WO 00/29535

PCT/US99/27200

1/4

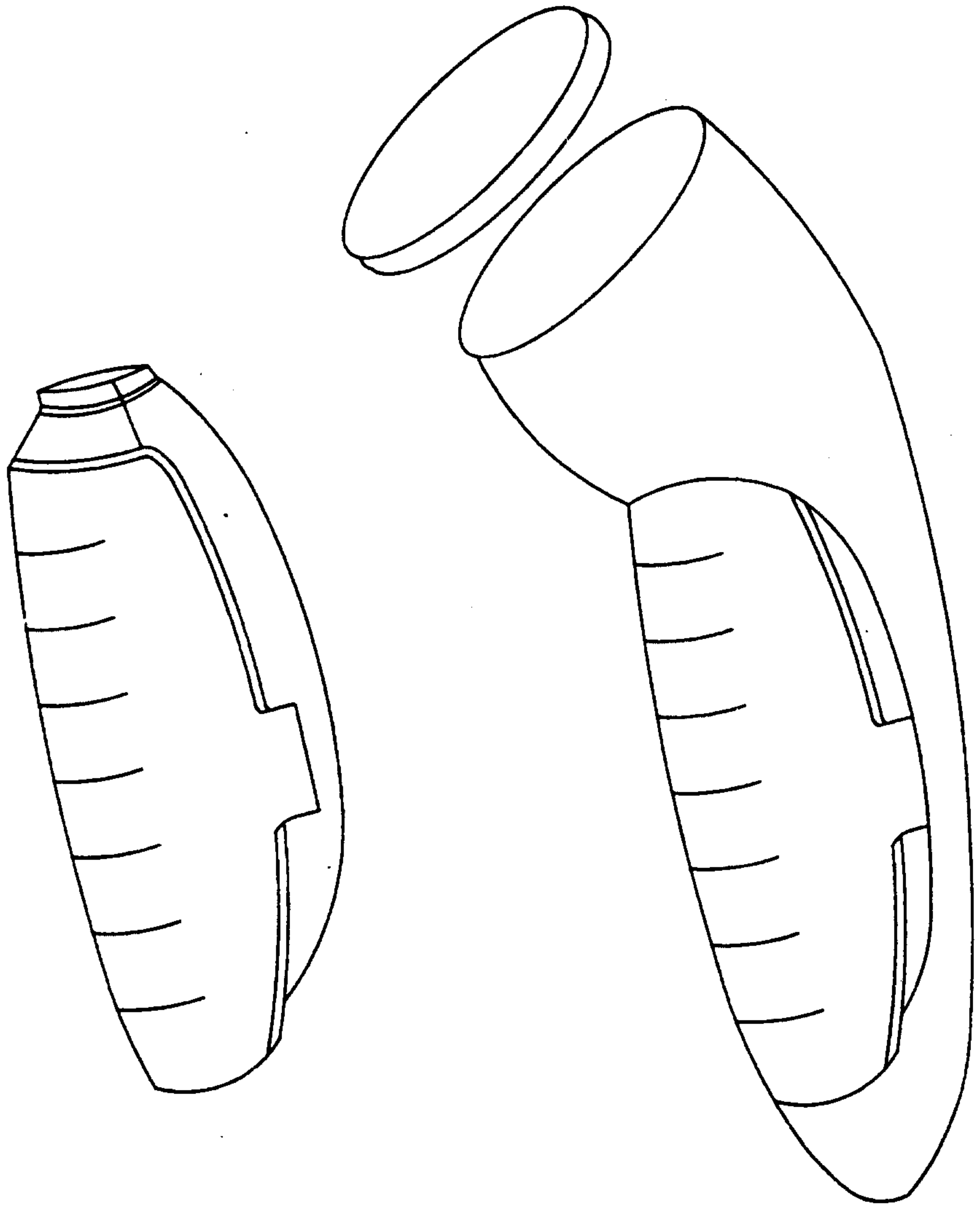


FIG. 1

2/4

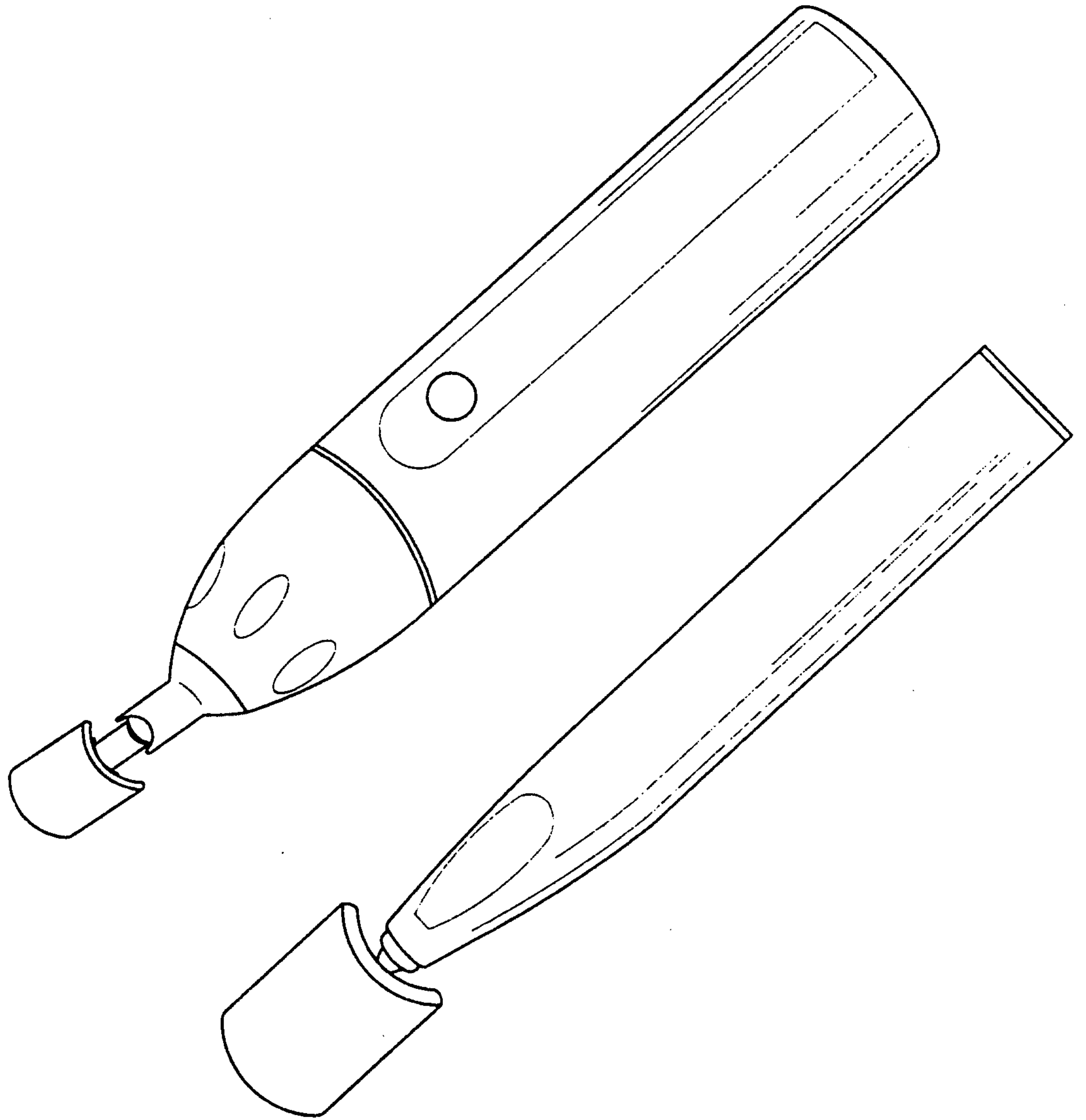


FIG. 2

3/4

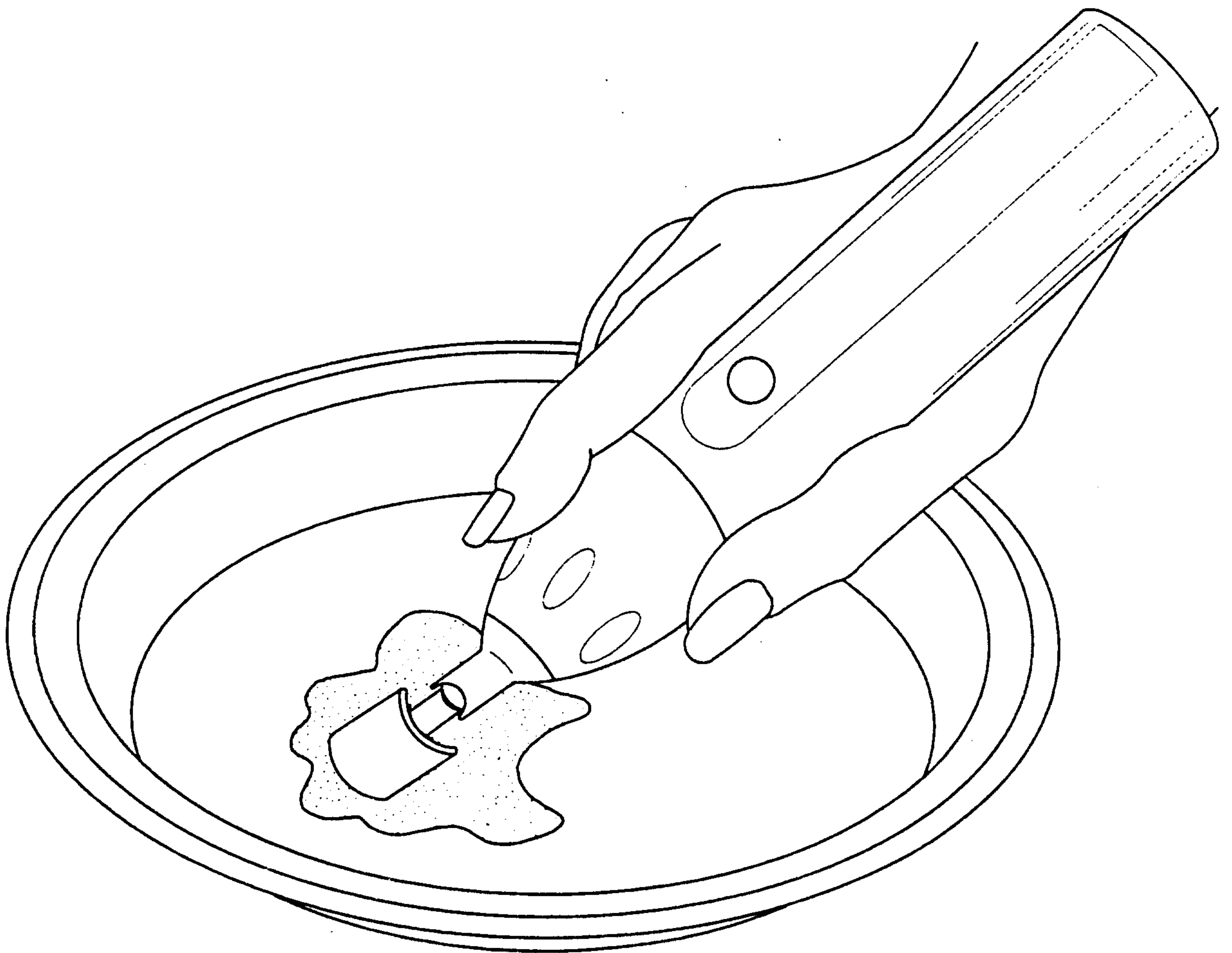


FIG. 3

WO 00/29535

PCT/US99/27200

4 / 4

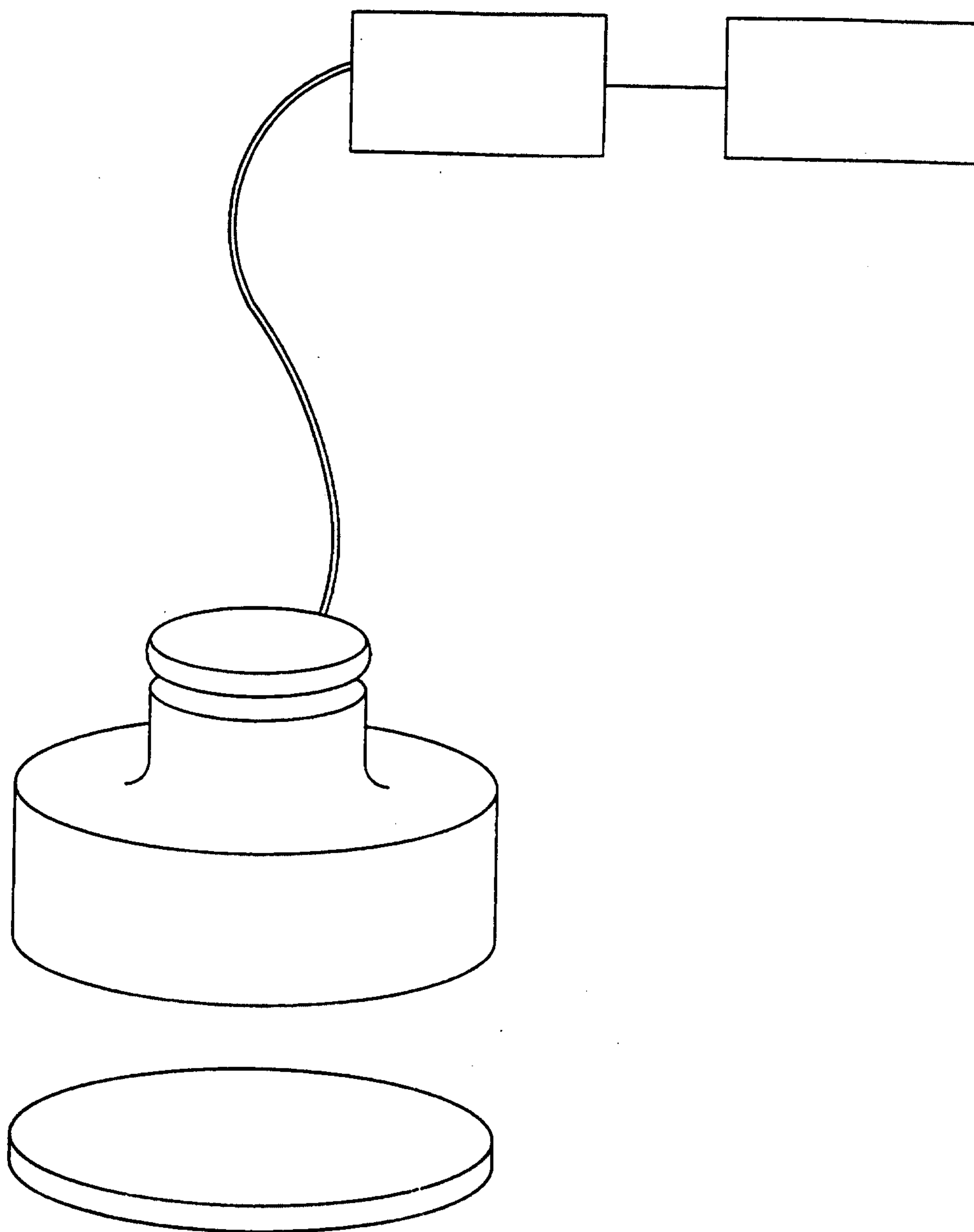


FIG. 4