

"N-ALKYL NEOALKANOAMIDES"

This invention relates to N-alkyl neoalkanamides, which are novel chemical compounds that possess insect and other pest repelling properties, and are useful components of perfumes. More specifically, this invention relates to N-lower alkyl neoalkanamides. The mentioned neoalkanamides, especially N-methyl and N-ethyl neodecanamides and neotridecanamides, have been found to be especially effective in repelling insects, such as German cockroaches, when applied to surfaces of structures, items and materials to be protected. The present invention also relates to various compositions containing such N-alkyl neoalkanamides, which compositions may be perfumes or may be insect repelling, employed as a means for depositing such active compounds onto surfaces to be made repellent to insects.

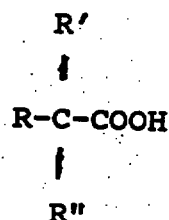
Some prior art insect repellent materials are toxic and others are foul smelling and discolouring, which adverse properties can seriously limit their utilities. Most of the useful insect repellents reported in the literature are tertiary amides and of these the one heretofore regarded as the most effective all-purpose insect repellent is N,N-diethyl-m-toluamide, which is often referred to as "DEET". However, the present neoalkanamides, and N-methyl neodecanamide and N-methyl neotridecanamide in particular, are superior to DEET in long lasting effectiveness, and in at least one entomological laboratory, have replaced DEET as the standard of repellent action (against roaches). Additionally, such neoalkanamides are also

1 effective to repel other insects, including mosquitoes,
2 and have been found to be of greater effectiveness
3 against Anopheles quadrimaculatus than DEET. In view
4 of the relatively small number of useful insect
5 repellents known, efforts continue to be made to
6 discover additional repellents which would be of
7 greater repellent actions and of longer lasting
8 effects. Desirably, such compounds also would be of
9 improved physical characteristics, such as of more
10 pleasant aroma, desirable volatility, non-staining
11 character, liquid state (preferable), improved
12 stability, greater substantivity to substrates, and
13 longer lasting repellent effect.

14 In accordance with one aspect, the present
15 invention extends to the use of an N-lower alkyl
16 neoalkanoamide in which the lower alkyl group is of 1
17 to 4 carbon atoms, preferably 1 to 2 carbon atoms, and
18 the neoalkanoyl moiety is of 7 to 14 carbon atoms,
19 preferably 9 to 13, as an insect repellent or a
20 perfume.

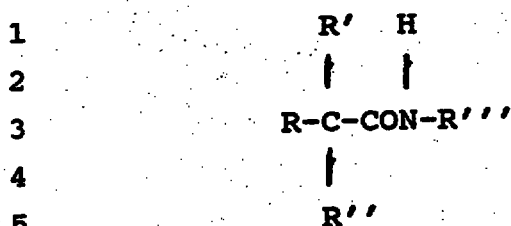
21 According to another aspect of the present
22 invention there are provided insect repellent
23 compositions or perfumes containing N-alkyl
24 neoalkanamides in which the alkyl thereof is of 1 to 4
25 carbon atoms preferably 1 or 2 carbon atoms, and the
26 neoalkanoyl moiety is of 7 to 14 carbon atoms,
27 preferably 9 to 13 or 9 to 11. The present invention
28 also extends to certain insect repellent N-alkyl
29 neoalkanamides per se, namely N-lower alkyl
30 neoalkanamides in which the lower alkyl is methyl and
31 the neoalkanoyl moiety is of 10, 11, 12 or 13 carbon
32 atoms, or in which the lower alkyl is ethyl and the
33 neoalkanoyl moiety is of 12 or 13 carbon atoms, and

1 specifically N-methyl neodecanamide, N-methyl
 2 neotridecanamide and N-ethyl neotridecanamide. A
 3 preferred form of the present invention provides an
 4 insect repellent N-lower alkyl neodecanamide which is
 5 made by reacting a primary alkyl amine of 1 to 4,
 6 preferably 1 or 2, carbon atoms with a neodecanoic acid
 7 which is made by reacting a corresponding alkene and
 8 carbon monoxide under high pressure and at elevated
 9 temperature in the presence of an aqueous acidic
 10 catalyst (Koch reaction) to produce a neodecanoic acid
 11 of the formula



17 wherein R, R' and R'' are alkyl groups and the total
 18 number of carbon atoms in R + R' + R'' is 8, in which
 19 about 31% of the neodecanoic acid is of a structure
 20 wherein R' and R'' are both methyl and R is hexyl, about
 21 67% of the neodecanoic acid is of a structure wherein
 22 R' is methyl, R'' is alkyl of a carbon atoms content
 23 greater than that of methyl and less than that of R,
 24 and R is of a carbon atoms content less than that of
 25 hexyl and greater than that of R'', and about 2% of the
 26 neodecanoic acid is of a structure wherein R' and R'' are
 27 both of a carbon atoms content greater than that of
 28 methyl and less than that of R, and R is of a carbon
 29 atoms content less than that of hexyl and greater than
 30 those of R' and R''.

31
 32 The invention also extends to N-alkyl neoalkyl
 33 neoalkanamides of the formula



wherein R, R' and R'' are alkyl groups and the total number of carbon atoms in R + R' + R'' is 8, in which about 31% of the neodecanoic acid from which the amide is made is of a structure wherein R' and R'' are both methyl and R is hexyl, about 67% of the neodecanoic acid is of a structure wherein R' is methyl, R'' is alkyl of a carbon atoms content greater than that of methyl and less than that of R, and R is of a carbon atoms content less than that of hexyl and greater than that of R'', and about 2% of the neodecanoic acid is of a structure wherein R' and R'' are both of a carbon atoms content greater than that of methyl and less than that of R, and R is of a carbon atoms content less than that of hexyl and greater than those of R' and R'', and R''' is an alkyl group of 1-4 carbon atoms.

The present invention also extends to an insect repellent composition or a perfume comprising an N-lower alkyl neoalkanoamide wherein the lower alkyl is of 1 to 4 carbon atoms and the neoalkanoyl moiety is of a number of carbon atoms in the range 7 to 14. At present one of the most preferred of such compounds for employment as an insect repellent, especially effective against German cockroaches, is methyl neodecanamide. Also within the invention are detergent compositions (both particulate and liquid), carpet and upholstery shampoos, human hair shampoos, hard surface cleaners, and soap and detergent bars comprising such N-alkyl

1 neoalkanamide(s). Also useful are solutions and
2 dispersions of the neoalkanamide(s) in liquid media or
3 the neoalkanamides dispersed in a particulate or
4 powdered carrier, which particulate or liquid products
5 are suitable for application to a location from which
6 insects are to be repelled. Also within the invention
7 are processes for repelling insects by applications of
8 insect repelling amounts of
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neoalkanamides of this invention to or near a surface, area, location or item from which such insects are to be repelled. In some situations the present repellents may be used in conjunction with insecticides, to repel the insects from one area and toward the location of the insecticide. Alternatively, they may be formulated with insecticides so that after the repellent effect is lost the treated area will still not be safe for insects.

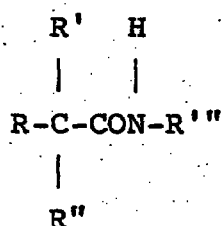
Perfumes of this invention in which such N-lower alkyl neoalkanamides are present comprise a N-lower alkyl neoalkanamide or a mixture of a plurality of such N-lower alkyl neoalkanamides, wherein the lower alkyl is of or averages 1 to 4 carbon atoms and the neoalkanoyl moiety thereof is of or averages 7 to 14 carbon atoms, and at least one perfume component which is of a type selected from the group consisting of essential oils, esters, ethers, aldehydes, alcohols, hydrocarbons, ketones and lactones, in which the content of such neoalkanamide(s) is in the range of 0.1 to 98%.

Computer and manual searches of the prior art have not resulted in the finding of any reports of volatile primary or secondary amides that were recognized to be perfume or repellent components. Such searches indicated that the N-lower alkyl neoalkanamides of the present invention are novel and unobvious. The closest compounds to the N-lower alkyl neoalkanamides of this invention appear to be those described in GB-A-2173792 (Colgate-Palmolive Co) published 22nd October 1986 which relates to N-higher alkyl neoalkanamides. However, the neoalkanamides of that patent application are taught therein to be useful as antistatic agents,

not as insect repellents. Also, such application had not been published as of the priority date of the present application.

The present alkyl neoalkanamide insect repellent or perfume compositions and processes include those wherein the alkyl is of 1 to 4 carbon atoms, more preferably one or two carbon atoms (methyl or ethyl), and often most preferably such will be methyl. The neoalkanoyl moiety, which may be derived from any of the suitable neoalkanoic acids, several of which are available commercially, will be of 7 to 14 carbon atoms (of a number of carbon atoms in the range of 7 to 14), such as neodecanoyl, neotridecanoyl or neoheptanoyl, and often will preferably be neodecanoyl. Among the available neoalkanoic acids are neopentanoic acid, neoheptanoic acid, neononanoic acid, neodecanoic acid, neododecanoic acid, neotridecanoic acid, and neotetradecanoic acid, and the corresponding alkyl neoalkanamides thereof, such as the methyl and ethyl neoalkanamides, may be made from such neoalkanoic acids. Usually the alkyl groups are straight chain but they can also branch. Pure neoalkanamides of the types described may be made but often the commercial or technical grade acids, which may be used, and the amides made from them, will be mixtures.

The amides are of the formula



wherein R, R' and R'' are alkyl groups, the sum of the

carbon atom contents of which is in the range of 5 to 12, and R'" is an alkyl, of 1 to 4 carbon atoms. Further details with respect to R, R' and R" will be given later, in conjunction with a description of neoalkanoic acids which may be employed as starting materials for the production of the neoalkanamides.

Infrared absorption spectra for some representative and preferred N-lower alkyl neoalkanamides of this invention are shown in the drawings, in which:

Figure 1 is an infrared absorption spectrograph of a sample of N-methyl neodecanamide;

Figure 2 is an infrared spectrograph of a sample of N-ethyl neodecanamide;

Figure 3 is an infrared spectrograph of a sample of N-methyl neoheptanamide; and

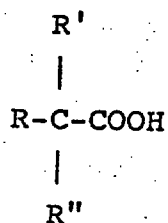
Figure 4 is an infrared spectrograph of a sample of N-methyl neotridecanamide.

Also shown in the drawings, in Figure 5, is a plot of insect repelling action vs. time, in which repellent effects of N-methyl neodecanamide and "DEET", a leading insect repellent, were compared.

To make the neoalkanamides of this invention neoalkanoyl chloride reactant is slowly reacted with the appropriate primary amine, in ethyl ether, after which reaction the reaction mixture is washed with distilled water, dilute hydrochloric acid solution, dilute sodium hydroxide solution, and more distilled water, until it is neutral to pH paper. The ether is then removed by means of a steam bath, followed by employment of a vacuum evaporator. The reaction product obtained is water white to light amber in colour and is essentially pure. In an alternative method, the neoalkanoic acid

may be reacted directly with the lower alkylamine.

Neoalkanoic acids, such as neodecanoic acid, neo-tridecanoic acid, neoheptanoic acid and neopentanoic acid, are available from Exxon Chemical Americas, which synthesizes them by reacting a suitable branched alkene and carbon monoxide under higher pressure at elevated temperature in the presence of aqueous acidic catalyst (Koch reaction). The general mechanism involved includes generation of carbonium ion, followed by complexation with carbon monoxide and the catalyst to form a "complex", which is subsequently hydrolyzed to generate free acid. The formula of the free acid is



In neodecanoic acid, for example, the total number of carbon atoms in R, R' and R" is 8, 31% of the neodecanoic acid is of a structure wherein R' and R" are both methyl and R is hexyl, 67% is of a formula wherein R' is methyl, R" is alkyl of a carbon atoms content greater than that of methyl and less than that of R, and R is of a carbon atoms content less than that of hexyl and greater than that of R"; and 2% is of the formula wherein R' and R" are both of a carbon atoms content greater than that of methyl and less than that of R, and R is of a carbon atoms content less than that of hexyl and greater than those of R' and R". Among other neoalkanoic acids that are available and useful to make the present amides may be mentioned others in the 7 to 14 carbon atoms content range, such as neoheptanoic, neononanoic, neodecanoic, neododecanoic,

neotridecanoic and neotetradecanoic acids. In the various neoalkanoic acids mentioned, when R is alkyl of five or more carbon atoms, such alkyl is branched. The acyl chloride starting materials for the reactions to produce the invented N-lower alkyl neoalkanamides may be made from the neoalkanoic acids and suitable chlorinating agents, such as phosphorous trichloride (although sometimes thionyl chloride may be found preferable), and are available from the Lucidol Division of Pennwalt, Inc. and from White Chemical Corp.

Although it is possible for the insect repellent compounds of this invention to be incorporated in various materials when such materials are being manufactured, as by being mixed in with pulp for making paper, rubber and synthetic organic polymeric plastic batches, and chips for the manufacture of pressed boards, and while the present insect repellent compounds may also be injected or otherwise inserted into the bodies of items to be made insect repellent, usually the insect repellents will be applied to surfaces of area, structures or items to be made insect repellent, either by direct application of the insect repelling N-alkyl neoalkanamide, in liquid solution or dispersion, or dispersed in a powdered carrier, or in a detergent composition, such as a laundry detergent, floor or wall cleaner, upholstery or rug shampoo, hair shampoo, liquid soap, bar soap, or in any other appropriate composition in which it may be usefully incorporated. Among such other appropriate compositions may be mentioned insecticidal and antibacterial washes or dips for humans, pets and farm animals, furniture polishes and finishes, floor waxes

and finishes, ointments, salves and topical medicaments, insecticides, fungicides, bactericides, plant fertilizers, mulches and plant potting preparations, to name only a few. In some instances means will be provided for recharging such items and compositions with the active alkanamide component to renew their repellent effects. In the majority of instances the invented compositions will be applied directly or indirectly by external application to surfaces to be treated, and afterward such application will be made on a continuing basis to maintain a satisfactory degree of insect repellency. Thus, the insect repellent N-alkyl neoalkanamide, such as N-methyl neodecanamide and/or N-methyl neotridecanamide, may be painted onto a surface to be treated or may be applied to such surface by washing it with a detergent composition containing the active insect repellent. The invented compounds are in liquid state or pasty condition at normal ambient temperatures and are water insoluble, so they tend to be satisfactorily substantive to surfaces from detergent compositions and from other preparations, even when such compositions are rinsed off, and normally, after either direct or indirect application to such surfaces, a sufficient amount of the alkanamide will remain to be effectively insect repelling. While different application rates of the different alkanamides of this invention are desirably used for effective repelling of different insects from different surfaces under different conditions, it is generally considered that insect repellent effects are obtainable at surface concentrations of the active ingredient in the range of 0.002 to 100 g./sq. m. For economic reasons and for effectiveness against such insects

there will normally be applied from 0.01 to 5 g./sq. m., preferably 0.1 to 2 g./sq. m., e.g. 1 g./sq. m., when roach repellency is desired. Higher application rates, such as 10 to 100 g./sq. m., will often be used against mosquitoes.

5 Because the present insect repellents are volatile their presence can be detected in the air near a surface to which they have been applied. Therefore, not only are the surfaces repellent to insects, which
10 will avoid having their body parts contact such surfaces, but the vapours from the N-lower alkyl neoalkanamides will tend to repel insects from the surrounding space. Thus, the application of the volatile repellent to walls of a china closet can repel
15 roaches from the closet interior, thereby preventing them from contacting, soiling and contaminating contained dishes, utensils and silverware. Similarly, coating of pantry surfaces, interior and/or exterior, with a furniture polish containing an invented volatile
20 repellent, or use of shelf paper containing a repellent neoalkanamide can discourage roaches from entering the pantry and contaminating foods contained therein. Also, washing of clothing with detergent compositions containing the invented repellents may prevent insects
25 from lighting on the clothing and its wearer, and from stinging or biting the wearer. Shampooing of a rug with a rug shampoo or carpet cleaner containing the invented repellent will discourage insects from entering the room and from nesting and laying their
30 eggs in or under the rug. Washing of floors and walls with insect repellent detergent compositions formulated for such purpose will deposit thereon a substantive coating of the invented insect repellent and will

discourage insects from contacting the floor and wall surfaces and from entering the treated rooms. It is an important feature of the invented insect repellents that although they are sufficiently volatile to be effective, their repellent properties are persistent, often lasting as long as three weeks or more (even longer if incorporated interiorly in a product). The invented repellents may be formulated with insecticides, such as by being sprayed onto the surfaces of insecticidal powders, e.g. boric acid powder, which is effective against roaches. By use of the neoalkanamide-boric acid composition immediate effectiveness in repelling the roaches is obtained and subsequently, after the repellent activity may have diminished, due to exhaustion by volatilization, any roaches that return to the area will be killed by the insecticide. It is recognized that a more normal practice is to incorporate an attractant with the insecticide but the repellent-insecticide composition also has utility.

It is apparent from the foregoing brief description that the invented insect repellents can be used in many compositions and can be applied in diverse ways. However, among the most useful products which can incorporate the invented neoalkanamides are detergent compositions, from which the neoalkanamides are surprisingly substantive to the surfaces of washed items. Such detergent compositions operate in several ways to counter insect contamination of the washed item. They remove any earlier contamination, remove stains and soils, on which the insects might feed, and which could attract them, and leave behind the insect repelling neoalkanamide.

The primary component of the present detergent

compositions, other than the insect repelling neo-alkanamide, is an organic detergent material. Such material may be one of the soaps, preferably a sodium and/or potassium higher (C₁₀₋₁₈) fatty acid soap, but is preferably a synthetic organic detergent, which may be of the anionic, nonionic, amphoteric, ampholytic, zwitterionic or cationic type, or may be a mixture of two or more detergents within one or more of such classifications. Preferably, the detergent will be a synthetic organic detergent of the anionic or nonionic type and often the anionic detergents will be most preferred. Descriptions of many such detergents are found in the text Surface Active Agents and Detergents, Vol.II, pages 25-138, by Schwartz, Perry and Berch, published in 1958 by Interscience Publishers, Inc. Such compounds are also described in a 1973 publication by John W. McCutcheon, entitled Detergents and Emulsifiers, and they form an art-recognized class known to those of skill in the art.

The anionic detergents employed may be any such suitable detergents (or soaps), but normally will be salts of alkali metals, such as sodium or potassium or ammonium or lower alkanolammonium salts, e.g. triethanolamine salts. The anionic detergent may be a sulphate, sulphonate, phosphate or phosphonate or salt of other suitable acid but usually will be a sulphate or sulphonate, which may be designated as "sulph(on)ate". Such anionic detergents will include a lipophilic group, which will normally have from 10 to 18 carbon atoms, preferably in linear higher alkyl arrangement, but other lipophilic groups may be present instead, preferably including 12 to 16 carbon atoms, such as branched chain alkyl benzene. In some cases

the anionic detergents may include poly-lower alkoxy groups, as in ethoxylated higher fatty alcohol sulphates, e.g. triethoxylated lauryl alcohol sulphate. Normally the number of ethoxy groups in such detergents will be in the range of 1 to 30, preferably 1 to 10. As examples of suitable anionic detergents there may be mentioned: higher fatty alcohol sulphonates, such as sodium tridecyl sulphonate; sodium linear alkyl benzene sulphonates, e.g. sodium linear tridecylbenzene sulphonate; olefin sulphonates; and paraffin sulphonates. All of the anionic detergents will preferably be sodium salts for most of the particulate detergent compositions of this invention but potassium, ammonium and triethanolammonium salts may be more desirable for some liquid compositions. Usually the detergent will preferably include a lipophilic alkyl moiety of 12 to 16 carbon atoms, often preferably of or averaging 12 to 13 carbon atoms.

The suitable nonionic detergents will normally be condensation products of lipophilic compounds or moieties and lower alkylene oxides or polyalkoxy moieties. Highly preferable lipophiles are higher fatty alcohols of 10 to 18 carbon atoms but alkyl phenols, such as octyl and nonyl phenols, may also be used. The alkylene oxide of preference is ethylene oxide and normally from 3 to 30 moles of ethylene oxide will be present per mole of lipophile.

In the built detergent compositions, in which builders are employed to improve the detergency of the synthetic organic detergent (or soap), there will be present a building proportion of a suitable builder. Builders used may be inorganic or organic, water soluble or water insoluble. Among such classes of

builders may be mentioned water soluble inorganic salts, including: polyphosphates, e.g. sodium tripolyphosphate; carbonates, e.g. sodium carbonate; bicarbonates, e.g. sodium bicarbonate; borates, e.g. borax; and silicates, e.g. sodium silicate; water insoluble inorganic builders, including zeolites, e.g. hydrated Zeolite 4A; and water soluble organic builders, including citrates, gluconates, NTA, and polyacetal carboxylates. In some cases, as when mildness of the product to the human body or to delicate fabrics is important, alkaline builders and other "harsh" builders will be avoided, and in many cases no builders will be present at all.

Various adjuvants may be present in the detergent compositions of this invention to improve various characteristics of such products. Thus, for example, bentonite may be employed as a fabric softener, perfumes and colourants may be added for their aesthetic effects, soil anti-redeposition agents may be employed, such as sodium carboxymethyl cellulose, and solvents or co-solvents may be present, as in liquid compositions. Among other adjuvants there may be mentioned fluorescent brighteners, antistatic agents, antibacterial agents, fungicides, foaming agents, anti-foams, flow promoters, suspending agents, antioxidants, anti-gelling agents, soil release promoting agents, and enzymes.

The detergent compositions of this invention may be in particulate, powder, tablet, bar, liquid, paste, gel, capsule, leaf, foam or "aerosol" or other suitable form, as may be best suited for the purpose intended. Methods for manufacturing products in such forms are well known in the art of processing soaps and

detergents, and need not be further mentioned here.

While it is possible to apply the present insect repelling N-lower alkyl neoalkanamides directly to surfaces and items to be made insect repellent, it is often more convenient and also more efficacious to utilize the repellent neoalkanamide as a liquid solution or emulsion, or as a liquid or particulate or powder dispersion. To make such solutions the neoalkanamide may be dissolved in any suitable solvent, such as a lower alcohol, e.g. ethanol, or in an aqueous alcoholic medium. Of course, other solvents may also be employed, such as hydrocarbons, esters, ketones, aldehydes and halogenated hydrocarbons. Among the hydrocarbons and halogenated hydrocarbons there may be mentioned isobutane and the chlorofluorinated lower hydrocarbons, such as dichlorodifluoromethane, monofluorotrichloromethane and other chlorofluoromethanes, -ethanes and -propanes. Such compounds include the liquifiable gases, which can be maintained in liquid state in pressurized dispensing containers, for ready application as sprays or in other suitable forms to locations which are to be made insect repellent. The neoalkanamides may also be in aqueous or other emulsion form, when a suitable emulsifier, hydrotrope or surface active agent is utilized, too. The invented neoalkanamides may also be dispersed in particulate or powdered inert or active materials. Among such inert materials may be mentioned silica, calcium carbonate, clay, expanded polystyrene, wood chips and sawdust. Also, the neoalkanamides may be dispersed in active materials, such as detergent composition beads, bentonite (a fabric softener) and boric acid) a roach poison).

Other modes of use of the invented insect repellents, some of which have already been mentioned, include incorporation in materials which are intended for use at or near sites from which the insects are to be excluded. Thus, the repellents may be incorporated in shelf papers, wallpapers, wallpaper glues, rugs and carpeting, and carpet padding. They may be formulated in floor waxes, furniture polishes and other preparations that are intended for applications to surfaces in the areas to be treated. They may be automatically dispensed in certain areas, such as storerooms and warehouses, by timer-operated sprayers or other dispensers, and they may be renewably charged to containers, from which they may be vaporized, such as absorbers and other holders, as in the under sides of garbage can covers.

The detergent compositions of this invention, including those that are useful for washing hard surfaces, such as floors, and also soft surfaces, such as those of carpets, laundry, and human hair, will include an insect repelling proportion of N-alkyl neoalkanamide or a mixture of such neoalkanamides, which proportion is sufficient so that enough of the neoalkanamide is retained on the washed surface, after washing of it with the detergent composition, to repel insects from such surface, and will also include a deterative proportion of soap or synthetic organic detergent (or any suitable mixture thereof). The neoalkanamide is preferably one wherein the lower alkyl is of 1 to 4 carbon atoms (and that designation includes mixed lower alkyls, too, averaging such numbers of carbon atoms), more preferably being methyl or ethyl, and usually most preferably being methyl.

The neoalkanoyl moiety of the neoalkanamide is of 7 to 14 carbon atoms, preferably 9 to 11 or 13 carbon atoms, and most preferably is of 10 carbon atoms. Mixtures of such neoalkanoyl moieties and "average" moieties, averaging within such ranges or averaging 10 to 13 carbon atoms also be used, and are to be considered as being within such descriptions. As was previously indicated, the more preferred neodecanamides are N-methyl and N-ethyl neodecanamides, of which N-methyl neodecanamide is most preferred, in most instances, although sometimes N-methyl neotridecanamide is preferred.

In particulate built laundry detergent compositions of the invention the active detergent component will usually be synthetic organic detergent selected from the group consisting of anionic, nonionic, amphoteric, ampholytic, and zwitterionic detergents and mixtures thereof, and the builder will be water soluble inorganic or organic builder or water insoluble inorganic builder. The proportions of synthetic organic detergent(s), builder(s), and neoalkanamide(s) to make an effective insect repellent particulate synthetic organic detergent composition will be 1 or 5 to 35%, 10 to 90%, and 0.2 to 10%, respectively. Preferred compositions of such type will have the synthetic organic detergent selected from the group consisting of anionic and nonionic detergents, and mixtures thereof, may contain water soluble filler salt(s), such as sodium sulphate, and will contain N-methyl neotridecanamide or neodecanamide, or a mixture thereof. The proportions of such components for best effects in such detergent compositions will often be 7 to 30% of the synthetic organic detergent(s), 20 to 75%

of the builder salt(s), 0 to 50% of the filler salt(s), and 0.5 to 5% of the neoalkanamide(s).

5 When liquid detergents containing the invented insect repellent neoalkanamide(s) are made, the same components may be used, plus a liquid medium, but the detergent will preferably be non-soap. Sometimes a conventional emulsifying agent, such as an Emcol (Registered Trade Mark), sold by Witco Chemical Co. Inc., will be employed, in emulsifying proportion. 10 Also, hydrotropes, such as sodium toluene sulphate, and other functional and aesthetic adjuvants, such as have been employed in liquid detergent compositions, and/or fillers, may be included, or not. In the built liquid detergents the synthetic organic detergent content will be in the range of 2 to 25%, the builder content will 15 be 5 to 40%, the neoalkanamide content will be 0.2 to 10%, and the liquid medium content, preferably aqueous, will be 40 to 90%. More preferably, the built liquid detergent compositions of the invention will comprise 3 to 20% of a synthetic organic detergent which is anionic and/or nonionic, 10 to 30% of builder salt(s) for such detergent(s), which may be water soluble, such as potassium pyrophosphate, sodium carbonate, or sodium 20 polyacetal carboxylate, and/or water insoluble, such as sodium zeolite, 0 to 20% of water soluble filler salt, such as sodium sulphate, 0.5 to 5% of N-methyl neodecanamide and/or N-ethyl neodecanamide, or other suitable neoalkanamide, and 50 to 90% of water, preferably deionized water. 25

30 When an insect repelling shampoo for use on upholstery, rugs and carpets is to be made, it may comprise 1 to 35%, preferably 5 to 20%, of a detergent selected from the group consisting of water soluble

5 soap(s) and synthetic organic detergents, 0 to 40% of
builder(s) for the soap and/or detergent, often
preferably 0%, and 0.2 to 10% of N-lower alkyl
neoalkanamide, preferably 0.5 to 5%, all being of the
broad types previously mentioned, in a liquid medium,
preferably aqueous, the percentage of which may be in
the range of 40 to 90%, preferably 70 to 90%, with
water being 50 to 90% of the composition, preferably 70
to 90%. Alternatively, the shampoo may be in gel,
10 paste or powder form.

When the present insect repellents are used in
shampoos intended for washing human hair on the head
and for making the hair repellent of insects, the
shampoos will preferably comprise 2 to 25% of soap
15 and/or the previously described synthetic organic
detergent(s), and 0.2 to 10% of N-lower alkyl
neoalkanamide, of the type previously discussed in
conjunction with the broad description of detergent
compositions, in an aqueous medium such as 40 to 90% of
20 water, preferably deionized water. The aqueous medium
may include up to half thereof of a co-solvent, such as
a lower alkanol, e.g. ethanol, or a glycol but normally
the percentage of such co-solvent will be limited to 5
to 25% of the final product. In more preferred embodi-
25 ments of the shampoos for human hair, there will be
present 5 to 22% of synthetic organic detergent, 0 to
20% of water soluble filler salt, 0.5 to 5% of N-lower
alkyl neodecanamide or mixture thereof, preferably N-
methyl neodecanamide or N-ethyl neodecanamide, and 50
30 to 90% of water, preferably deionized.

Solid or bar or cake insect repellent detergent
products can also be made, which may be used for
washing persons, animals, laundry, rugs, and/or hard

surfaces, such as walls and floors, to make them insect repellent. Such products can comprise neoalkanamide repellent with soap and/or synthetic organic detergent, or may also include builders, fillers and other adjuvants, previously referred to herein. The proportion of N-alkyl neoalkanamide in such products will normally be from 0.2 to 10%, and that of the deterative material will be from 15 to 95%. Such bars will normally be of a moisture content in the range of 2 to 20% and the balance will be of builder(s) and/or filler(s) and/or adjuvant(s), when such are present. Normally, the adjuvant(s) content of the various detergent products will be in the range of 0.5 to 20%, total, with individual adjuvants being 0.1 to 5% for the most part.

The various detergent compositions described above may be prepared by processes that are well known in the art and need not be described at length herein. Such processes include spray drying, dry mixing, spray applying and/or coating, sequential dissolving and/or dispersing and/or emulsifying, milling, plodding and pressing.

When the insect repellent is to be sprayed or applied in a carrier, such as a liquid or particulate material or medium, the concentration of it therein will be an insect repellent proportion, so that when applied onto a surface of a material to be treated (or into the interior or other portion thereof), by spraying, dusting, rubbing, wiping, pouring, depositing, or other mechanism, the repellent applied will be in such quantity and/or concentration that it will be effective in repelling insects or a particular type of insect, so that such insect(s) will stay away

from the treated location. Such repelling is due to the insect being reluctant to contact the repellent and also in some measure is due to the repellent effect of the vapour from the repellent, which is at least partially volatile, although it may last for as long as two weeks or more, as normally applied, using the application concentrations that were previously given. Also, the lasting power of the repellent is increased when it is incorporated in the body of an article, such as in a mattress or absorbent sponge, rather than only on a surface that is exposed to the air.

The concentration of the repellent chemical(s) in a liquid medium, such as an aqueous medium, in which a dispersing agent or emulsifier may be employed, too, will usually be in the range of 0.2 to 10, 25 to 50%, but is often preferably in the range of 0.5 to 10%, e.g. about 1% or 5%, for roach repellency. The liquid medium may be water, lower alkanol, such as ethanol, lower ketone, such as acetone, lower hydrocarbon, such as isobutane, cyclopropane or mixture thereof, or halogenated lower hydrocarbon, such as chlorofluorinated, fluorinated or chlorinated lower hydrocarbons, e.g. Propellants 11 and 12. The various "lower" compounds are of 1 to 4 carbon atoms per molecule, preferably 1 or 2 carbon atoms, and in the case of those that are normally in the gaseous state, they are under sufficient pressure to maintain them in liquid state.

Similar concentrations of the invented repellents may be employed in powdered or particulate carriers. Thus, the invented neoalkanamides may be applied as by spraying of liquid droplets onto powdered calcium carbonate, silica, clay or boric acid, onto grains of such materials, or onto detergent composition particles

or synthetic organic polymer beads (preferably of particle sizes between 125 microns and 2.4 mm in diameters), in concentrations in the range of 0.2 to 10 or 25%, preferably 0.5 to 5 or 10%, for roach repellents.

5 In insect repelling processes or treatments in which the invented repellents are employed they will normally be applied to surfaces to be treated at concentrations such that 0.002 to 100 g./sq. m. initially remain on such surfaces after treatment, with
10 such application rate preferably being 0.01 to 5 or 10 g/sq. m. and more preferably 0.1 to 2 g/sq. m., e.g. 1 g./sq. m. for action against roaches. Concentrations outside such ranges may sometimes also be of at least
15 partial effectiveness. When the repellent is in a detergent composition which is employed in an aqueous washing medium, such as water, the wash water will usually contain from 0.05 to 5% of the detergent composition but in some applications, such as
20 shampooing of human hair or of carpets or rugs with foam preparations, the concentration may be greater, sometimes being as high as 25%.

When the repellents are incorporated in and applied to surfaces in other media or preparations, such as waxes or furniture polishes, the concentrations
25 thereof will usually be in the same ranges as for detergent compositions, but may be increased, if desired, in some such instances to as high as 25%.

The invented repellents possess various significant advantages over various other repellent materials
30 available. They are essentially non-toxic and therefore are not hazardous to children or pets that might come into contact with them, after application. They

are pleasantly aromatic (sometimes fruity, with N-methyl neodecanamide and N-ethyl neodecanamide resembling apples and pears in odour) and therefore do not usually adversely affect the aromas of preparations into which they are formulated. In fact, they may be useful in giving such preparations acceptable aromas, and thereby permit the omissions of expensive perfumes from such products. They are substantially colourless and therefore can be employed in detergents, shampoos, polishes, sprays, and various compositions and preparations wherein the imparting of colour would not be acceptable. They are effective both as contact and vapour repellents and are superior in repelling action to various commercial insect repellents, especially against German cockroaches, which are considered to be the most difficult household insect pest to control. The present repellents are long lasting, with tests having shown both N-methyl neotridecanamide and N-methyl neodecanamide to be effective to repel roaches for two weeks and more after topical application. Against Anopheles quadrimaculatus N-methyl neodecanamide is effective for five weeks, by U.S. Dep't. of Agriculture screening tests (a week longer than DEET). Against Aedes aegypti the neoalkanamide is almost as effective as DEET, using the same test. The N-alkyl neoalkanamides are sufficiently stable to be able to maintain their insect repelling properties despite being incorporated in various soap, detergent, polish, wax, insecticide, cosmetic, and coating preparations, in liquid, paste, gel, foam, powder, particulate or solid bar form, or in aqueous or other solvent solutions, emulsions or dispersions, and they are highly substantive from such media.

Experimental work to date has proven conclusively that members of the class of N-alkyl neoalkanamides, wherein the alkyl is lower alkyl and the neoalkanoyl moiety is 7 to 14 carbon atoms, are superior insect repellents, being especially effective against both the German cockroach and the American cockroach, and evaluations of such compounds indicate that they will also be effective repellents against other insects, such as those in the group of flies, fleas, lice, mosquitoes, bees, wasps, hornets, ants and beetles, and they may also be effective against arachnids, such as spiders, ticks and mites. Because data are most complete and are very convincing for the use of N-methyl neodecanamide against German cockroaches, and because such data were obtained from controlled tests, conducted in connection with entomological research at a major university, such data, together with some mosquito repellency data, will be that presented in most of the working examples, which will follow.

In the perfume composition aspect of this invention the perfumes made contain N-lower alkyl neoalkanamide(s) which modify the fragrance of the perfume, is substantive to surfaces to which the perfume is applied, is satisfactorily stable on storage and in contact with alkaline media, and increases the strengths of aromas of various other perfuming components. In accordance with that aspect of the invention a novel liquid perfume, suitable for perfuming soaps and detergent compositions, comprises a N-lower alkyl neoalkanamide or a mixture of a plurality of such N-lower alkyl neoalkanamides, wherein the lower alkyl is of 1 to 4 carbon atoms and the neoalkanoyl moiety thereof is of 7 to 14 carbon atoms, and at least

one and preferably a plurality of perfume component(s) of type(s) selected from the group consisting of essential oils, esters, ethers, aldehydes, alcohols, hydrocarbons, ketones and lactones, in which the content of such neoalkanamide(s) is from 0.1 to 98%. Also within the invention are various household products that have been perfumed with the described perfume. Such products include built and unbuilt soap and synthetic organic detergent compositions, in particulate, liquid, gel, paste, bar or cake, and other acceptable forms, hard surface cleaning detergent compositions, hair shampoos, rug and upholstery shampoos, floor polishes and waxes, furniture polishes and waxes, and shelving papers. Also within the invention are synthetic organic polymeric "plastic" products containing a perfume of the invention, such as pet care articles, e.g. food dishes, bed frames, grooming aids, of perfumed plastic, and of other materials.

The described N-lower alkyl neoalkanamides are normally liquids and are of sufficient volatilities and lasting effects to be effective perfume materials. They are of pleasing aromas and are relatively long lasting. Additionally, they interact with other perfume components and often strengthen and otherwise improve the aromas of such components in the total perfume. A preferred neoalkanamide, N-ethyl neodecanamide, is of a mild, somewhat rose-like fragrance, with a slight plum or apple fruitiness. The fragrance of a drop, on a perfumer's blotter strip, is still noticeable after two weeks. N-methyl neodecanamide possesses a light, fresh, fruity pear-like aroma with floral undertones. Its fragrance is also still detectable

after two weeks. N-ethyl neoheptanamide has a "green", fruity, wine-like odour, which lasts one or two days, and N-methyl neoheptanamide has a fresh, clean, camphor-type odour, which also lasts one or two days. Other N-lower alkyl neoalkanamides of the class described herein are also aromatic and persistent, and tend to be substantive to surfaces to which they are applied. Additionally, they are generally of satisfactory stabilities in a wide variety of preparations, even those which may be of substantial alkalinities.

With the N-lower alkyl neoalkanamide(s) component(s) of the present perfumes there may be employed any of the various well-known aromatic perfuming components, fixatives, solvents, extenders, stabilizers and adjuvants. Of these the primarily perfuming materials will often fall in one or more of the following classes: essential oils, esters, ethers, aldehydes, alcohols, hydrocarbons, ketones, and lactones, but various other classes of materials may also be present, such as pyrrones, and pyrroles.

Among preferred components of rose, lily, tropical fruit and floral-woody-amber type perfumes are the following: essential oils - citrus, evergreen, jasmine, lily, rose, ylang ylang; esters - phenoxyethyl isobutyrate, benzyl acetate, p-tertiary butyl cyclohexyl acetate, guaiacwood acetate, linalyl acetate, dimethylbenzyl carbonyl acetate, phenylethyl acetate, linalyl benzoate, benzyl formate, ethymethylphenyl glycidate, allylcyclohexane propionate, styrallyl propionate, and benzyl salicylate; ethers - benzylethyl ether; aldehydes - alkyl aldehydes of 8 to 18 carbon atoms, bourgeonal, citral, citronellal, citronellyl oxyacetal-

dehyde, cyclamen aldehyde, hydroxy citronellal, and lillial; alcohols - anethol, citronellol, eugenol, geraniol, linalool, phenylethyl alcohol and terpeneol; hydrocarbons - balsams and terpenes; ketones - ionones, alpha-isomethyl ionone, and methylcedryl ketone; lactones - gamma-alkyl lactone wherein the alkyl is of 8 to 14 carbon atoms; pyrrones - hydroxy lower alkyl pyrrone wherein the alkyl is of 1 to 4 carbon atoms; and pyrroles - benzopyrrole.

Although the components mentioned above are preferred in perfumes of the invention for producing the types of fragrances previously mentioned, various other perfumery materials may also be employed, including lemon oil, lime oil, orange oil, bergamot oil, sweet orange oil, petitgrain bigarade oil, rosemary oil, dimethyl anthranilate, indole, methyl anthranilate, jasmine oil, patchouly oil, vetiver bourbon oil, vanillin, ethyl vanillin, coumarin, 3-methyl nonan-3-yl-acetate, methyl ionone, synthetic lily of the valley oil, synthetic red rose oil, 3-methyl nonan-3-ol, alpha-amyl cinnamic aldehyde, methyl salicylate, amyl salicylate, lavandin, isobutyl heptenone, cedryl acetate, ethyl inalyl acetate, neryl acetate, nerol, d-limonene, cuminic aldehyde, linalyl propionate, nerolidyl acetate, nerolidyl formate, alpha-pinene, isobutyl linalool, methylnaphthyl ketone, linalyl isobutyrate, paracresyl caprylate, paracresyl phenylacetate, sandalwood oil, coriander oil, sassafras oil, cassia oil, angelica root oil, Peruvian balsam, clove oil, mace oil, menthol, and almond oil.

In addition to the named fragrance components there may also be employed fixative type materials, including musk, civet, castoreum, ambergris, gum

benzoin, musk ambrette, musk ketone, musk xylol, oleoresin orris root, resinoid benzoin Siam and resinoid opopanax, as well as various other resins, gums, synthetic musks and other fixatives. Also components of perfumes are alcohols and other suitable solvents and media, as well as preservatives, antioxidants, stabilizers and viscosity and volatility modifiers.

The perfumes and perfuming materials of this invention may contain from 0.1 to 98% of N-lower alkyl neoalkanamide(s), with the balance thereof being other fragrance materials and perfume constituents, which may include solvents, liquid media and/or particulate or powder bases, such as wood particles, sachet materials and clays. Preferably the perfume will be in liquid state, more preferably in a lower alcoholic solvent, e.g. ethanol, and the concentration of N-lower alkyl neoalkanamide therein will be in the range of 1 to 60%. More preferably, such concentration will be in the range of 2 to 30% and most preferably it will usually be in the range of 5 to 15%, e.g. 10%. Normally, the proportion of fixative(s) will be less than that of the fragrance material, and will usually be in the range of 0.1 to 5%. The proportion of solvent may be variable but will usually be from 20 to 95%, preferably 50 to 90%, and may be omitted entirely from some perfumes which are to be employed as concentrates, as when the perfume is added to a product or composition, rather than being a handkerchief perfume.

Although the proportions of the various non-N-methyl neoalkanamide fragrance components of the perfume are variable, with individual components ranging from 0.01 to 30% in some cases, and sometimes

with certain of the classes of such materials being omitted from the formulas, normally there will be present in most perfume formulas at least one ester, at least one aldehyde and at least one alcohol representative of the fragrance classes. The proportions of each of such classes will usually be at least 1%, with at least one of such classes being present to the extent of at least 5% and sometimes at least 10%. However, in other instances one or more of the three mentioned classes of fragrance components may be omitted, as in preferred floral-woody-amber perfumes which may comprise from 5 to 40% of citrenellol, 5 to 30% of geraniol and 2 to 40% of phenylethyl alcohol, with such proportions preferably being in the ranges of 5 to 20%, 5 to 25% and 2 to 15%, e.g. 8%, 10%, and 5%, respectively. The total of non-N-ethyl neoalkanamide fragrance components present in the invented perfumes will usually be in the range of 5 to 99%, preferably 50 to 90%, with the greater percentages being present in the concentrates (from which solvent is omitted).

The proportion of perfume (usually as non-solvent concentrate) employed in various household and other products of this invention will usually be from 0.1 to 10%, preferably 0.5 to 5% and frequently 1 to 3%, with the content of N-lower alkyl neoalkanamide normally being within the range of 0.01 to 5%, preferably 0.1 to 2% and often 0.2 to 1%. However, in perfuming, odourant or air freshening sprays the range of concentrations of perfume may be increased to 5 to 25% and even to as high as 50%, and sometimes the perfume concentrate may be employed undiluted.

The invented perfumes may be usefully employed in a wide variety of household products and in various

other components and articles. Representative of these are detergent compositions of various types, insect repellents, insecticides, paper items, textiles, surface treating compositions and synthetic organic polymeric "plastic" articles. The detergent compositions include built and unbuilt particulate, liquid, gel, paste and bar or cake detergents, such as are employed as laundry detergents, rug shampoos, human hair shampoos, upholstery cleaners, and hard surface cleaners (including scouring cleansers and wall and floor cleaners). The insect repellent compositions may be in liquid, gel, paste, powder or other suitable form, as may be insecticides perfumed with the present compositions, although the insecticides will normally be in liquid solvent or liquified gas solution or emulsion. From the above it is seen that the N-lower alkyl neoalkanamides can contribute both perfuming and insect repelling properties to various household products.

The following examples illustrate but do not limit the invention. Unless otherwise stated, all parts are by weight and all temperatures are in °C, in such examples, and elsewhere in this specification and in the appended claims.

EXAMPLE 1

N-methyl neodecanamide was made from methyl amine and neodecanoyl chloride in a reaction conducted in a 3-necked glass one-litre flask equipped with a Chesapeake stirrer, a thermometer, an additional funnel (a dropping funnel) and a condenser equipped with a Drierite (Registered Trade Mark) desiccant tube. The flask was placed in an ice bath and was charged with 31 grams of methyl amine, 700 ml of diethyl ether and 59

grams of triethyl amine (which functioned to remove from the reaction mixture any HCl that was produced). Then 190.5 grams of neodecanoyl chloride (obtained from Pennwalt Corporation's Lucidol Division) were added dropwise to the flask over a period of one hour. After completion of the addition of the neodecanoyl chloride the reaction mixture was allowed to come to room temperature. The reaction mixture was then transferred to a 2-litre separatory funnel and was washed twice with deionized water to separate the N-methyl neodecanamide from the triethylamine chloride, once with 5% aqueous hydrochloric acid, and once with 5% aqueous sodium hydroxide, after which it was further washed with distilled water until the washings were neutral to litmus paper. The ether was then removed from the mixture by heating it on a steam bath, followed by finishing such removal with a rotary vacuum evaporator. The reaction product resulting, in essentially stoichiometric yield, is N-methyl neodecanamide. It was distilled at 235°C under 760 mm Hg. The result is a pure, water white product. An infrared spectrograph of the product is shown in Figure 1.

In similar manner there were made N-ethyl neodecanamide, N-methyl neotridecanamide, N-ethyl neotridecanamide, N-methyl neoheptanamide and N-ethyl neoheptanamide, using gram-molar weights of the appropriate alkyl amine (ethyl amine, methyl amine, ethyl amine, methyl amine and ethyl amine, respectively), triethylamine, and neoalkanoyl chloride (neodecanoyl chloride, neotridecanoyl chloride, neotridecanoyl chloride, neoheptanoyl chloride and neoheptanoyl chloride, respectively). The same volume of diethyl

ether (700 ml) is employed as in the preparation of the N-methyl neodecanamide, the same equipment is used, and the same procedures of addition, reaction, separation, washing, evaporation and distillation are followed.

5 The products are obtained in essentially stoichiometric yields. Some of their infrared spectrographs are shown in Figures 2 to 4.

EXAMPLE 2

10 The six compounds for which manufacturing methods are described in Example 1, are made, but the starting materials which act as sources of the neoalkanol moieties are the corresponding neoalkanoic acids instead of the acid chlorides, and no triethyl amine is employed. In such reactions, in which stoichiometric
15 proportions of neoalkanoic acid and alkyl amine are employed, with diethyl ether as the reaction solvent, a one-litre 3-necked flask is also used but the system is closed (to avoid loss of alkyl amine) and the flask is equipped with a heating mantle, a magnetic stirrer, a
20 source of nitrogen gas with means for conveying it to below the surface of the reaction mixture, and a thermometer and thermostatic control to regulate the temperature of the reaction mixture, which is held at 240°C for five hours. The reaction products are
25 separated, washed and have ether removed from them in the same manner as described in Example 1. The products resulting have infrared spectrographs like those of the samples of corresponding products of Example 1, which are shown in Figures 1 to 4.

EXAMPLE 3

30 The N-methyl neodecanamide made by the process of Example 1 was tested for cockroach repellency by dissolving one gram of it in 10 ml of acetone and then

swabbing the inside of a Dixie (Registered Trade Mark) cup, having an internal surface area of 188.5 sq cm, with the solution so that upon evaporation of the acetone there is left behind 0.0189 g of the N-methyl neodecanamide, evenly coating the cup interior at a concentration of 1.0 g/m². Four equidistant openings, are cut in the drinking end edges of the cup so that when the cup is inverted and placed on a flat surface, it will be possible for test insects (roaches) to crawl through them and under it. An identical control cup is prepared, with the sole difference being that the same proportion of acetone is applied to the cup and floor surface but no N-methyl neodecanamide is present with it. Each cup is placed in the middle of a half of a medially dividable rectangular area in a box, to which there are next added 100 cockroaches. The box top is transparent and the roaches cannot escape from the box. Initially the box is in the dark but to test the effectiveness of the repellent applied to the cup interior the box is illuminated with a 100 watt incandescent bulb positioned about 50 cm above it. Each of the roaches, seeking to hide from the light, crawls under one of the inverted cups. It is considered that any significant difference in the number of roaches under the experimental and control cups indicates repellency or attraction effected by the experimental cup because the control is essentially neutral, having nothing remaining on its surfaces. After waiting one minute after illumination, a divider is slid across the box, separating the experimental and control areas, the cups are removed or knocked over, and the roaches in each section are counted. The number in the control area is the percentage effectiveness of the repellent.

By this test, after two days, N-methyl neodecanamide is 100% effective against the control. After two days, when N-methyl neodecanamide (NMNDA) is compared to DEET, and to a successful cockroach repellent, identified as MGK-874, the N-methyl neodecanamide (NMNDA) is rated to be 9 times and 19 times as effective, respectively, as the other repellents. After five days after application of the repellent to the surfaces mentioned, a similar test shows the experimental NMNDA repellent to be even more effective, and such comparative effectiveness is still exhibited after 14 days. However, after 21 days none of the experimental and comparative repellents is of much repellent effect so comparisons after that time are not considered to be significant.

Figure 5 is a graph showing comparative effectiveness (in %) of N-methyl neodecanamide and DEET in repelling roaches. The number of roaches hiding under the DEET treated cup is plotted for each of the indicated days after the applications of the repellents. The comparative effectiveness of the experimental compounds, NMNDA, in %, is the number (out of 100) of roaches hiding under the DEET cup.

In a variation of the described test only the inner bottom parts (the upper parts when the cups are inverted) are coated with the various test, control, and comparison materials, at the same concentration, 1.0 g/m. The results are of the same type and order as described above for the contact repellency tests but the absolute effectivenesses of the experimental products are less than for the contact tests, as would be expected, due to the lesser quantities of repellents applied and the facts that the repellents were not on

the lower and side surfaces of the cups, which the roaches are more prone to occupy, so that repellent action is more due to a vapour effect than to contact.

In the described tests results are the same whether the repellents are made by the direct condensation method, from neoalkanoic acids, or from the neoalkanoyl chlorides. Similar results are obtainable when other neoalkanamides of the invented types are employed, such as N-ethyl neodecanamide, N-butyl neodecanamide, N-methyl neotridecanamide, N-ethyl neotridecanamide, the N-methyl- and N-ethyl- neoheptanamides, -neononanamides, neoundecanamides, and neododecanamides, and best contact and vapour repellency effects are obtained when the neoalkanamides are those which are normally in liquid state under atmospheric conditions, and are volatile enough to have the vapours thereof detectable to insects, and repugnant to them.

Instead of applying the repellents to the test surfaces in acetone solution they may be sprayed onto such surfaces by means of "aerosol" or pressurized sprays in 50:50 mixture of isobutane and cyclobutane or 60:40 solutions of Freon (Registered Trade Mark) 12 and Freon 11 (dichlorodi-fluoromethane and trichloromonofluoromethane, respectively) or in other pressurized solvents. Instead of applying the solution at the concentration in the tests reported earlier in this example, concentrations in the range of 2% to 30% may often be used, depending to some extent on the solubility of the repellents in the solvent system employed, for example 15% in the Freon system, 20% in the hydrocarbon system, 5% in ethanol, and 25% in methyl ethyl ketone. Aqueous systems may also be used, preferably with emulsifiers or suitable surface active agents being present to hold

the repellent in homogeneous suspension as colloidal droplets, with its concentration usually being somewhat lower than for the organic solvent solutions, e.g. 3%, 5% and 7%. All such liquid systems may be applied with the aids of cloths, pads, spray cans and nozzles, and gels or pastes can also be used.

In practical tests, on actual kitchen floors, counters, drainboards and walls, and in kitchen cabinets and dishwashers, and under refrigerators, in roach-infested apartments, significantly fewer roaches will be observed on surfaces to which or near which the invented repellents are applied than on control surfaces, and fewer roaches are found on the bottoms and shelves of cabinets and pantries when walls thereof are treated with the invented repellents, especially when the repellent is N-methyl neodecanamide or N-methyl neotridecanamide, indicating that the repellents are vapour-effective too, as well as contact-effective. When floors, walls, counters, sinks, cabinets, appliances, windows, doors, rugs and carpets in the house or apartment are treated with the invented repellents, e.g. N-methyl neodecanamide, N-ethyl neodecanamide or N-methyl neotridecanamide, the incidence of cockroach infestation is reduced, compared to control apartments where no repellent is applied. However, because of the initial presence of the pests in the premises, control of them may take as long as a week or two, and sometimes can require several applications of the repellent. In some instances the application rates are desirably increased to as high as 10 g/sq.m. but in other instances such rates may be dropped to 0.01g/sq.m. or lower. Of course, results are usually better with higher application rates.

EXAMPLE 4

5 N-methyl neotridecanamide (NMNTDA) was made from neotridecanoyl chloride and methyl amine by the method described in Example 1 for the manufacture of N-methyl neodecanamide, using stoichiometrically adjusted proportions of the acid chloride and the amine. The neotridecanoyl chloride starting material was made from neotridecanoic acid, obtained from Exxon Chemical
10 Americas, which identifies such acid by the designation ECR-903. Such neotridecanoic acid is a mixture of neo-acids of 12 to 14 carbon atoms, averaging about 13. It has an acid value of about 273 and a specific gravity, at 20°C, of 0.9117 g/cu.cm. The N-methyl neotridecanamide resulting is purified by the method described in
15 Example 1 and yields the infra-red spectrograph of Figure 4.

The N-methyl neotridecanamide made possesses a faint, pleasant tobacco-like odour. When tested for insect repellency, according to the procedure described
20 in Example 3, N-methyl neotridecanamide was found to be as good as or better than N-methyl neodecanamide against German cockroaches, showing an average of about 14 days effectiveness at a 100% repellency level, and about 25 days effectiveness at a 60% repellency level,
25 whereas comparable average test results for N-methyl neodecanamide are about 11 days and 17 days, respectively.

When the N-ethyl neodecanamide is made, employing essentially the same synthesis, but with ethyl amine reactant, it, too, is tested for insect repelling
30 characteristics but is found to be significantly less effective in this respect than the N-methyl neotridecanamide.

EXAMPLE 5

5 N-Methyl neodecanamide (NMNDA), dissolved at a suitable concentration, e.g. 10%, in acetone, is applied to a cotton stocking so that 1 g. of the neo-
10 alkanamide is on 280 sq. cm. of stocking. Two hours after treatment of the stocking (during which period the acetone volatilizes off) the stocking is pulled over a previously installed nylon stocking on the arm of a human test subject and that so-covered arm is
15 exposed in a cage of adult mosquitoes of a type against which DEET is an effective repellent. Two such species are Aedes aegypti and Anopheles quadrimaculatus. If fewer than five mosquitoes bite the subject through the stocking during a one-minute exposure the test is
20 repeated 24 hours later, and if fewer than five mosquitoes then bite the subject the test is repeated weekly thereafter until five bites are received within a one-minute exposure period. The degree of repellency of a treatment chemical or composition is measured by
the number of days from application of the chemical to the stocking until five mosquitoes bite the test arm within the one-minute exposure period.

25 In the described test against Aedes aegypti DEET is rated 22 and NMNDA is rated 15, and when the test mosquito is Anopheles quadrimaculatus the rates are 29 and 36, respectively. Thus, the present N-lower alkyl neoalkanamide is about equivalent to the DEET standard in mosquito repellency, as measured by the described
30 Agricultural Research Service (U.S. Department of Agriculture) screening test, as employed by their Insects Affecting Man and Animals Research Laboratory at Gainesville, Florida.

In actual use on the human body, to which it is

applied dissolved in a suitable solvent, in a skin lotion or cream, or in an "aerosol" spray, the NMNDA will be about equivalent to DEET, giving at least an hour's protection against Aedes aegypti and Anopheles quadrimaculatus when 0.3 g. is applied to a human forearm. Similar results are obtainable with other alkyl neoalkanamides, such as N-ethyl neodecanamide, N-methyl neotridecanamide, N-ethyl neotridecanamide, N-methyl neononanamide and N-ethyl neoundecanamide, and mixtures of two or more thereof.

EXAMPLE 6 (Built particulate Detergent)

<u>Component</u>	<u>Percent</u>
Sodium linear tridecyl benzene sulphonate	20.0
Sodium tripolyphosphate	40.0
15 Sodium carbonate	10.0
Sodium bicarbonate	10.0
Borax	5.0
Enzyme blend (proteolytic + amylolytic in powdered carrier)	1.0
20 Sodium carboxymethylcellulose	0.5
Fluorescent brightener	1.0
N-methyl neodecanamide	2.0
Water	<u>10.5</u>
	100.0

25

All of the components of the detergent composition except the enzyme powder and repellent are mixed together in a crutcher slurry, which is spray dried to hollow globular bead form, of particle sizes in the range of No's. 10 to 100, U.S. Sieve Series. Subsequently, the enzyme powder is blended with the spray dried beads and the insect repellent, in liquid state, is sprayed onto the mixture, while it is being tumbled,

30

to form a uniform composition. N-methyl neotridecanamide can be substituted for the NMNDA, if desired, and clothes washed will be more insect repellent than control laundry.

5 EXAMPLE 7 (Scouring Cleanser)

<u>Component</u>	<u>Percent</u>
Silex (finely divided silica powder)	97.5
Sodium linear dodecyl benzene sulphonate	2.0
N-ethyl neodecanamide	0.5
	<hr/>
	100.0

10 EXAMPLE 8 (Built Liquid All-Purpose Detergent)

<u>Component</u>	<u>Percent</u>
15 Nonionic detergent*	1.0
Sodium linear dodecyl benzene sulphonate	2.0
Sodium cumene sulphonate	5.0
Sodium carbonate	5.0
Sodium bicarbonate	1.0
20 Fluorescent brightener	0.02
Dye	0.01
N-methyl neononanamide or N-methyl neodecanamide	1.0
Water (deionized)	84.97
25	<hr/>
	100.0

* Condensation product of 1 mole of higher fatty alcohol mixture averaging 10 carbon atoms, with 5 moles of ethylene oxide.

30

EXAMPLE 9
 (Built Liquid All-Purpose Cleaner)

<u>Component</u>	<u>Percent</u>
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Sodium linear dodecylbenzene sulphonate	3.7
Sodium sulphate	3.3
Natural soda ash	4.0
Sodium bicarbonate	2.0
Nonionic detergent*	2.0
Isopropyl alcohol	1.8
Distilled coconut oil fatty acids	0.5
Dyes (as 0.1% aqueous solutions)	0.6
Perfume	0.8
Softened water	80.3
N-methyl neotridecanamide	1.0
	100.0

* Condensation product of one mole of a mixture of higher fatty alcohols of 9-11 carbon atoms, with 6 moles of ethylene oxide.

The pH of the insect repellent liquid all-purpose cleaner is adjusted with either sulphuric acid or caustic soda to be 10.5 ± 0.2 .

The product made is an effective insect repellent cleaner, and surfaces and articles washed with it or to which it is applied, as a concentrated or diluted product, are left with a minor proportion of N-methyl neotridecanamide insect repellent thereon, so such surfaces and articles become insect repellent.

EXAMPLE 10

(Liquid Pine Oil Cleaner)

<u>Component</u>	<u>Percent</u>
Sodium paraffin sulphonate	6.8
Isopropanol	7.0
Neodol (Registered Trade Mark)	
23-6.5 (Shell Chemical Corporation)*	4.0
Pine Oil	10.0

CLAIMS

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2
3 1. The use of an N-lower alkyl neoalkanamide in
4 which the lower alkyl group is of 1 to 4 carbon atoms
5 and the neoalkanoyl moiety is of 7 to 14 carbon atoms
6 as an insect repellent.

7
8 2. The use of an N-lower alkyl neoalkanamide in
9 which the lower alkyl group is of 1 to 4 carbon atoms
10 and the neoalkanoyl moiety is of 7 to 14 carbon atoms
11 as a perfume.

12
13 3. The use of an N-lower alkyl neoalkanamide
14 in which the lower alkyl group is of 1 or 2 carbon
15 atoms and the neoalkanoyl moiety is of 9 to 13 carbon
16 atoms as an insect repellent.

17
18 4. The use of an N-lower alkyl neoalkanamide
19 in which the lower alkyl group is of 1 or 2 carbon
20 atoms and the neoalkanoyl moiety is of 9 to 13 carbon
21 atoms as a perfume.

22
23 5. An insect repellent N-lower alkyl
24 neoalkanamide wherein the lower alkyl is methyl and the
25 neoalkanoyl moiety is of 10, 11, 12 or 13 carbon atoms.

26
27 6. An insect repellent N-lower alkyl
28 neoalkanamide wherein the lower alkyl is ethyl and the
29 neoalkanoyl moiety is of 12 or 13 carbon atoms.

30
31 7. N-methyl neodecanamide.
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1 8. N-methyl neotridecanamide.

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3 9. N-ethyl neotridecanamide.

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5 10. N-alkyl neoalkyl neoalkanamides of the
6 formula

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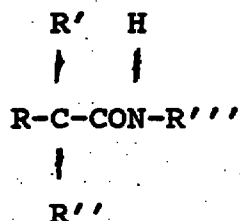
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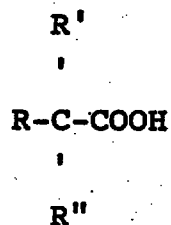
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wherein R, R' and R'' are alkyl groups and the total number of carbon atoms in R + R' + R'' is 8, in which about 31% of the neodecanoic acid from which the amide is made is of a structure wherein R' and R'' are both methyl and R is hexyl, about 67% of the neodecanoic acid is of a structure wherein R' is methyl, R'' is alkyl of a carbon atoms content greater than that of methyl and less than that of R, and R is of a carbon atoms content less than that of hexyl and greater than that of R'', and about 2% of the neodecanoic acid is of a structure wherein R' and R'' are both of a carbon atoms content greater than that of methyl and less than that of R, and R is of a carbon atoms content less than that of hexyl and greater than those of R' and R'', and R''' is an alkyl group of 1-4 carbon atoms.

11. An insect repellent N-lower alkyl neodecanamide which is made by reacting a primary alkyl amine of 1 or 2 carbon atoms with a neodecanoic acid which is made by reacting a corresponding alkene and



carbon monoxide under high pressure and at elevated temperature in the presence of an aqueous acidic catalyst (Koch reaction) to produce a neodecanoic acid of the formula



wherein the total number of carbon atoms in $\text{R} + \text{R}' + \text{R}''$ is 8, in which about 31% of the neodecanoic acid is of a structure wherein R' and R'' are both methyl and R is hexyl, about 67% of the neodecanoic acid is of a structure wherein R' is methyl, R'' is alkyl of a carbon atoms content greater than that of methyl and less than that of R , and R is of a carbon atoms content less than that of hexyl and greater than that of R'' , and about 2% of the neodecanoic acid is of a structure wherein R' and R'' are both of a carbon atoms content greater than that of methyl and less than that of R , and R is of a carbon atoms content less than that of hexyl and greater than those of R' and R'' .

12. An insect repellent composition comprising an N-lower alkyl neoalkanamide wherein the lower alkyl is of 1 to 4 carbon atoms and the neoalkanoyl moiety is of a number of carbon atoms in the range of 7 to 14, or an N-lower alkyl neoalkanamide as claimed in any one of Claims 5 to 10.



13. A perfume comprising an N-lower alkyl neoalkanamide wherein the lower alkyl is of 1 to 4 carbon atoms and the neoalkanoyl moiety is of a number of carbon atoms in the range of 7 to 14, or an N-lower alkyl neoalkanamide as claimed in any one of Claims 5 to 10.

14. A detergent composition suitable for washing hard or soft surfaces and for making them insect repellent which comprises a deterative proportion of soap or synthetic organic detergent, and an insect repelling proportion of N-alkyl neoalkanamide, wherein the alkyl is of 1 to 4 carbon atoms and the neoalkanoyl moiety is of 7 to 14 carbon atoms, said insect repelling proportion of said N-alkyl neoalkanamide being sufficient so that enough is retained on such surface, after washing with the detergent composition, to repel insects from such surface.

15. A laundry detergent composition according to Claim 14 which is particulate.

16. A detergent composition as claimed in claim 14 or 15 comprising 1 to 35% of a synthetic organic detergent selected from anionic, nonionic, amphoteric, ampholytic and zwitterionic detergents, and mixtures thereof.

17. A detergent composition as claimed in claim 14, 15 or 16 comprising 10 to 90% of builder(s) for the detergent(s).



18. A detergent composition as claimed in any one of claims 14 to 17, comprising 0.2 to 10% of N-lower alkyl neoalkanamide or a mixture of such N-lower alkyl neoalkanamides

19. A detergent composition according to Claim 16 comprising 7 to 30% of a synthetic organic detergent selected from anionic and nonionic detergents, and mixtures thereof.

20. A detergent composition as claimed in claim 16 comprising 20 to 75% of water soluble and/or water insoluble builder salts for the detergent(s).

21. A detergent composition as claimed in any one of claims 14 to 20 comprising 0 to 50% of water soluble filler salt.

22. A detergent composition as claimed in claim 21 comprising 0.5 to 5% of N-lower alkyl neoalkanamide or a mixture of such N-lower alkyl neoalkanamides wherein the number of carbon atoms in the lower alkyl(s) is/are in the range of 1 to 2.

23. A detergent composition according to Claim 14 which is liquid and wherein the number of carbon atoms in the neoalkanoyl moiety of the N-lower alkyl neoalkanamide is in the range of 9 to 11.

24. A liquid detergent composition according to Claim 17 comprising 3 to 20% of a synthetic organic detergent selected from the group consisting of anionic and nonionic detergents, and mixtures thereof, 10 to



30% of water soluble and/or water insoluble builder salts for such detergents, 0 to 20% of water soluble filler salt, 0.5 to 5% of N-methyl neodecanamide, and 50 to 90% of water.

25. A detergent composition according to Claim 14, which is a shampoo for washing human hair and for making it repellent of insects, comprising 2 to 25% of a synthetic organic detergent selected from anionic, nonionic, amphoteric, ampholytic and zwitterionic detergents, and mixtures thereof, and 0.2 to 10% of N-lower alkyl neoalkanamide or a mixture of such N-lower alkyl neoalkanamides, in an aqueous medium.

26. A detergent composition according to Claim 14, which is a rug shampoo for cleaning rugs and/or carpets and for making them repellent of insects, comprising 1 to 35% of a detergent selected from water soluble soap and synthetic organic detergent(s) selected from the group consisting of anionic, nonionic, amphoteric, ampholytic and zwitterionic detergents, and mixtures thereof, 0.2 to 10% of N-lower alkyl neoalkanamide or a mixture of such N-lower alkyl neoalkanamides, and 0 to 40% of builder(s) for the detergent, in a liquid medium.

27. A solid pest repellent detergent product in bar or cake form for washing persons, animals, laundry, rugs and/or hard surfaces and making them repellent to insects, which comprises soap and/or synthetic organic detergent and an insect repelling proportion of N-alkyl



* C L H S *

neoalkanamide, wherein the alkyl is of 1 to 4 carbon atoms and the neoalkanoyl moiety is of 7 to 14 carbon atoms.

28. A solid detergent product according to Claim 27 wherein the deterative component is selected from synthetic anionic, nonionic, amphoteric, ampholytic and zwitterionic detergents, and mixtures thereof, and the N-alkyl neoalkanamide is one wherein the alkyl is of 1 to 4 carbon atoms and the neoalkanoyl moiety is of 9 to 11 carbon atoms.

29. A solid detergent product according to Claim 27 wherein the deterative component is a soap of a mixture of higher fatty acids of carbon atom contents in the range of 10 to 18, and the N-alkyl neoalkanamide is one wherein the alkyl is of 1 to 4 carbon atoms and the neoalkanoyl moiety is of 9 to 11 carbon atoms.

30. A pest repellent composition which comprises an insect repellent proportion of N-alkyl neoalkanamide wherein the alkyl is of 1 to 4 carbon atoms and the neoalkanoyl moiety is of 7 to 14 carbon atoms, dispersed or dissolved in a liquid medium.

31. A pest repellent composition according to Claim 30 wherein the alkyl of the N-alkyl neoalkanamide is of 1 or 2 carbon atoms.

32. A pest repellent composition according to claims 30 or 31 wherein the neoalkanoyl moiety of the N-alkyl neoalkanamide is of 9 to 11 carbon atoms.



* C L M S *

33. A pest repellent composition according to claim 30, 31 or 32 wherein the N-alkyl neoalkanamide is dispersed in an aqueous medium at a concentration in the range of 0.2 to 50%.

34. A pest repellent composition according to any one of claims 30 to 33 wherein the N-alkyl neoalkanamide is dissolved in a liquid solvent medium at a concentration in the range of 0.2 to 25%.

35. A pest repellent composition according to any one of claims 30 to 34 wherein the N-alkyl neoalkanamide is N-methyl or N-ethyl neodecanamide.

36. A pest repellent composition according to any one of claims 30 to 35 wherein the concentration of the N-alkyl neoalkanamide in the liquid solvent medium is in the range of 0.5 to 10%.

37. A pest repellent composition according to any one of claims 30 to 35 wherein the solvent medium is a normally gaseous hydrocarbon or halogenated hydrocarbon under sufficient pressure to be in liquid state at room temperature.

38. A process for repelling insects from an area, location or item which comprises applying to or near such area, location or item an insect repelling quantity of N-alkyl neoalkanamide(s), wherein the alkyl is of 1 to 4 carbon atoms and the neoalkanoyl moiety is of 7 to 14 carbon atoms.



39. A process according to Claim 38 wherein the alkyl of the neoalkanamide is of 1 or 2 carbon atoms and the neoalkanoyl moiety thereof is neodecanoyl.

40. A process according to Claim 38 or 39 wherein the neoalkanamide is applied to the area, location or item by washing such area, location or item with a detergent composition which comprises a deterative proportion of soap or synthetic organic detergent, and an insect repelling proportion of N-lower alkyl neoalkanamide(s), wherein the lower alkyl is of 1 to 4 carbon atoms and the neoalkanoyl moiety is of 9 to 11 carbon atoms, said insect repelling proportion of said N-lower alkyl lower neoalkanamide(s) being sufficient so that enough is retained on the washed area, location or item, after washing with the detergent composition, to repel insects from such area, location or item.

41. A process according to Claim 38, 39 or 40 wherein the N-alkyl neoalkanamide(s) application rate is in the range of 0.2 to 10 g/sq. m.

42. A perfume which comprises N-lower alkyl neoalkanamide or a mixture of a plurality of such N-lower alkyl neoalkanamides, wherein the lower alkyl is of or averages 1 to 4 carbon atoms and the neoalkanoyl moiety thereof is of or averages 7 to 14 carbon atoms, and at least one perfume component which is of a type selected from essential oils, esters, ethers, aldehydes, alcohols, hydrocarbons, ketones and lactones, in which the content of such neoalkanamide(s) is in the range of 0.1 to 98%.



43. A perfume according to Claim 42 which is in liquid state, and wherein the neoalkanoyl moiety of the N-lower alkyl neoalkanamide is of 7 to 14 carbon atoms, the content of neoalkanamide(s) in the perfume is in the range of 1 to 60%, and the neoalkanamide(s) is/are in mixture with a plurality of perfume components of a plurality of the types listed in Claim 38.

44. A perfume according to Claim 43 wherein the lower alkyl(s) of the neoalkanamide(s) is/are of 1 to 2 carbon atoms, the neoalkanoyl moiety/moieties thereof is/are of 9 to 11 carbon atoms, and the content of neoalkanamide(s) in the perfume is in the range of 2 to 30%.

45. A perfume according to Claim 44 wherein the N-lower alkyl neoalkanamide is N-methyl- and/or N-ethyl neoalkanamide and the content thereof in the perfume is in the range of 5 to 15%.

46. A perfume according to any one of Claims 42 to 45 which comprises at least 1% of each of such ester, aldehyde and alcohol classes of perfume components.

47. A perfume according to Claim 45 or 46 wherein the N-lower alkyl neoalkanamide is N-ethyl neodecanamide and the balance of the perfume comprises 5 to 40% of citronellol, 5 to 30% of geraniol and 2 to 40% of phenylethyl alcohol.



48. A household product which is a particulate detergent composition, a toilet soap, in bar or cake form, a liquid laundry detergent composition, a detergent composition for cleaning hard surfaces, a shampoo composition for shampooing hair, an upholstery shampoo, a rug shampoo, a floor polish, a furniture polish, an insect repellent, an insecticide or a scouring cleanser, which is perfumed with 0.1 to 10% of a perfume according to Claim 42.

49. An N-lower alkyl neoalkanamide as claimed in any one of claims 5 to 10 substantially as herein described with reference to any one of the Examples.

50. A detergent composition substantially as herein described with reference to any one of the Examples.

51. A solid pest repellent detergent product substantially as herein described with reference to any one of the Examples.

52. A pest repellent composition substantially as herein described with reference to any one of the Examples.

53. A process for repelling insects substantially as herein described with reference to any one of the Examples.

54. A perfume composition substantially as herein described with reference to any one of the Examples.

55. A household product substantially as herein described with reference to any one of the Examples.

