Patented Aug. 18, 1953

2,649,473

UNITED STATES PATENT OFFICE

2,649,473

SUBSTITUTED CARBAMIC ACID ESTERS AS SURFACE ACTIVE AGENTS

Joseph A. Chenicek, Bensenville, Ill., assignor to Universal Oil Products Company, Chicago, Ill., a corporation of Delaware

No Drawing. Application December 28, 1950, Serial No. 203,207

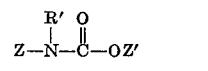
1 Claim. (Cl. 260—482)

1

This invention relates to certain non-ionic compounds useful as surface active agents and detergents and to an operable process for their manufacture. More specifically, the invention concerns certain N-aliphatic substituted carbamic acid esters of specific structure containing a hydrophilic group and a hydrophobic radical having such mutual effect in solution that the hydrophilic and hydrophobic properties substantially balance each other, as requisite to micelle formation and surface activity.

It is well known and widely recognized in the detergent art that the capacity of a particular compound to act as a surface active agent or a detergent in solution with an appropriate solvent depends upon the ability of the compound when dissolved in a solvent miscible therewith to orient itself in solution to form micellar aggregates in which the hydrophobic portion of one molecule aligns itself with the hydrophobic portion of another molecule of the same compound in solution, the hydrophilic portions of the several molecules in the micelle (usually at least several hundred in number) likewise becoming aligned in adjacent positions to form an aggregate of a large number of such molecules, which as a unit is referred to as a "micelle." The products of the present invention are novel applications of the theory of detergency in which the hydrophilic group is a poly-oxyalkylene chain of sufficient length to provide a radical having hydrophilic properties and the hydrophobic portion comprises a long-chain aliphatic alkyl group of sufficient length to impart a degree of water repellency to the molecule of detergent sufficient in effect to balance the hydrophilic properties of the molecule and provide that critical internal balance between the hydrophilic and hydrophobic portions requisite to detergency. The respective alkyl and poly-oxyalkylene chain are substituents of a carbamic acid ester which serves as the structural foundation for the detergent molecule.

In one of its embodiments, the present invention concerns a non-ionic detergent comprising a compound having the empirical structural formula:



wherein Z is selected from the group consisting of (—OR)$_x$OH and R'' and Z' is selected from the remaining member of said group, R is an alkylene group containing from 2 to about 5 carbon atoms per group, R' is selected from the

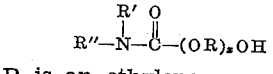
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group consisting of hydrogen, alkyl and substituted alkyl, R'' is an aliphatic alkyl group containing from about 8 to about 25 carbon atoms per group, and x is a whole number having a value of from about 2 to about 25.

Another embodiment of the invention concerns a process for the production of a surface active agent which comprises condensing a substituted amine containing at least one and not more than two N-substituents selected from the group consisting of (—OR)$_x$OH and R' with a halocarbonic acid ester containing an alkoxy radical selected from the group consisting of (—OR)$_x$OH and OR' wherein x is a whole number having a value of from 2 to about 25, R is an alkylene group containing from 2 to 5 carbon atoms per group and R' is an alkyl group containing from about 8 to about 25 carbon atoms per group, said process being further characterized in that not more than one (—OR)$_x$OH group and not more than one R' group is present in the same molecule of surface active agent.

Still another embodiment of this invention relates to a process for the production of a non-ionic surface active agent comprising an N-substituted carbamic acid ester in which the N-substituent is an aliphatic organic radical, which comprises condensing a di-alkyl amine with a poly-oxyalkylene glycol ester of chloroformic acid, said di-alkyl-amine being further characterized in that one of the N-alkyl substituents is an aliphatic hydrocarbon group containing from 8 to about 25 carbon atoms per alkyl group and the other of the N-alkyl substituents of said di-alkyl-amine is an aliphatic hydrocarbon group containing from 1 to about 5 carbon atoms per molecule, and said glycol ester of chloroformic acid is further characterized in that said poly-oxy-alkylene glycol ester contains from about 2 to about 25 oxyethylene groups per molecule.

A further embodiment of the invention, relating to one of the preferred species of the present non-ionic surface active agents, concerns a compound represented by the empirical formula:



wherein R is an ethylene group, x is a whole number having a value of from about 10 to about 15, R'' is an aliphatic alkyl group containing from about 12 to about 18 carbon atoms per group, and R' is an alkyl group containing from 1 to 5 carbon atoms per group.

The surface active and wetting agents of the present invention, some of which act as deter-

gents in aqueous or non-aqueous solutions, are considered broadly as a species of the generic class of compounds characterized as N-substituted carbamic acid esters of aliphatic alcohols and the specific series of compounds herein specified as surface active agents are represented by the empirical formulae:

(1) $$HO(RO-)_xR-\underset{\displaystyle R'}{\underset{|}{N}}-C-OR''$$

and

(2) $$R''-\underset{\displaystyle R'}{\underset{|}{N}}-C-(OR)_xOH$$

wherein R in both the above (1) and (2) series of compounds is an alkylene group containing from 2 to 5 carbon atoms per group, R' is selected from the group consisting of hydrogen, alkyl and substituted alkyl groups, R'' is an aliphatic alkyl group containing from 8 to about 25 carbon atoms per group, and x is a whole number having a value of from 2 to about 25. In each case, the R'' group acts as the hydrophobic portion of the molecule while the remaining portion of the molecule, and particularly the polyalkylene glycol chain, acts in the capacity of the hydrophilic portion, each portion balancing the effect of the other by the proper selection of the component alkyl and polyoxyalkylene groups present in the molecular structure.

The above series of surface active products may be prepared by any convenient means available which produce compounds of the indicated structure. A readily available method of manufacture, generally preferred for the preparation of the present products, comprises condensing an ester of a haloformic acid with a poly-substituted amine at reaction conditions resulting in a metathasis-type of reaction between the halogen atom of the haloformic acid ester and a hydrogen atom or alkyl group of the poly-substituted amine, the reaction liberating the corresponding hydrogen halide or alkyl halide and forming a carbamic acid ester as the primary condensation product.

The products of the present series of surface active agents represented by Formula 1, above, and herein designated as an N-polyoxyalkylene-substituted carbamic acid ester of an aliphatic alcohol are prepared by means of a reaction involving at least two stages, the number of stages required depending upon the reactants available as starting materials. The reaction mechanism involved in their preparation involves essentially the condensation of an N-polyoxyalkylene substituted amine with a haloformic acid ester of a long chain alcohol. Since not generally available in prepared form, the amine reactant is synthesized prior to the primary condensation reaction by reacting an amine such as ammonia, a mono-alkylamine or dialkylamine with a polyoxyalkylene glycol or alkylene oxide containing from 2 to 5 carbon atoms per alkylene group, the glycol reactant and the reaction conditions being selected to form an amine containing an hydroxy-polyoxyalkylene substituent having at least 2, up to about 25 alkylene groups per molecule. The reaction is a condensation-type mechanism and is carried out at temperatures of from about 10° to about 100° C., preferably from about 30° to about 80° C., and desirably in the presence of an acid-acting catalyst, present in the reaction mixture in an amount more than sufficient to neutralize the amine reactant. Superatmospheric pressures are generally desirable in this reaction to maintain the reaction mixture substantially in liquid phase during the course of the condensation reaction, particularly when the reactants are volatile at the temperatures utilized in the condensation reaction. A preferred means for effecting the reaction comprises bubbling the alkylene oxide in its gaseous form into a quantity of the ammonia, mono- or dialkylamine maintained in liquid form at the desired reaction temperature and at superatmospheric pressures, if required, to maintain liquid phase conditions. Suitable catalysts for the condensation reaction include the strong mineral acids, such as hydrochloric, sulfuric, and phosphoric acids, certain inorganic acid-acting materials, such as the normally acidic alumina-silica composites, a composite of silica and phosphoric acid, known generally in the art as a "solid phosphoric acid catalyst" and other materials well known as acid-acting substances. It is to be noted that when utilizing a mono-alkylamine in the preparation of the hydroxy-polyoxyalkylene-substituted amine, and when suitable reaction conditions are selected which tend to enhance the condensation of more than one poly-oxyalkylene group with the amine, a di- or tri-polyoxyalkylene substituted amine may be prepared which may be preferred for the manufacture of highly water-soluble surface active agents and detergents. The formation of the di-(polyoxyalkylene)-substituted amine is generally favored at relatively high reaction temperatures, whereas the preferred mono-(polyoxyalkylene)-substituted amine condensation product is formed by the condensation of an alkylene oxide or a polyalkylene glycol with a di-alkylamine under reaction conditions generally less severe (at temperatures, for example, of from about 0° to about 50° C.) than for the preparation of the poly-(polyoxyalkylene)-substituted amines.

The alkylene oxides and the polyoxyalkylene glycols utilizable in the condensation reaction with the mono- or dialkylamine to form the corresponding N-substituted polyoxyalkylene amines are selected from the above reactants in which the alkylene group contains from 2 to about 5 carbon atoms per alkylene group, including such alkylene oxides as ethylene-oxide, a propylene-oxide (such as trimethylene oxide or methyl-ethylene oxide), a butylene oxide (such as iso-butylene oxide), and amylene oxide and such polyoxyalkylene glycols as polyethylene glycol, polypropylene glycol, a polybutylene glycol, and a polyamylene glycol. Since the polyoxyalkylene groups in the molecular structure of the present detergents and wetting agents constitute the hydrophilic portion of the molecule, it is evident that for the final product to be water-soluble, the number of water-solubilizing polyoxyalkylene groups present in the compound, relative to the size and effect of the hydrophobic group, must predominate; for the preparation of such water-soluble products, therefore, the total molecular weight of the polyalkylene glycol must be large and the number of oxyalkylene groups per molecule must also be relatively large. Thus, the shorter the chain length of the alkylene group of the polyoxyalkylene radical, the greater is the water-solubilizing capacity of the radical for a given molecular weight, and therefore, the polyethylene and polypropylene glycols are the preferred polyalkylene glycol reactants. The number of oxyalkylene units per molecule of polyalkylene glycol reactant is preferably at least 5

and is desirably from about 10 to about 20 for the polyethylene and polypropylene glycols.

For the production of relatively water-insoluble surface active agents and detergents, on the other hand, products which may be utilized in non-aqueous systems, for example, the polyalkylene glycol or polyalkylene oxide utilizable in the condensation reaction with the amine is preferably selected from the polypropylene, polybutylene and polyamylene species, the solubility of the ultimate product tending to decrease as the chain length of the alkylene group increases beyond 2 carbon atoms, although low molecular weight polyethylene glycols, generally containing less than about 5 oxyethylene units per molecule, do not contain a sufficient number of water-solubilizing oxyalkylene groups to produce a water-soluble product and the latter polyethylene glycols, therefore, may be utilized when a product soluble in organic solvents, but relatively insoluble in water, is preferred.

The primary condensation of the N-polyoxyalkyleneamine, prepared as indicated above in a preliminary stage of the process, and an alkylhaloformate takes place in accordance with a reaction mechanism in which an alkyl group or hydrogen atom substituent on the amino nitrogen atom is replaced by the carbonic acid ester radical through the displacement of the halogen atom of the haloformate ester and the liberation of hydrogen halide or alkylhalide from the reaction via the resulting condensation. Since in the Series (1) compounds of this invention the alkoxy group of the formate ester contains the hydrophobic alkyl group essential for detergency of the ultimate product, the chain length of the alkoxy group must be sufficient to impart hydrophobic properties to the alkoxy radical; it has been found that such hydrophobic properties sufficient to balance the hydrophilic properties of the polyoxyalkylene group, are present in alkoxy radicals containing from about 8 to about 25 carbon atoms per group. Suitable alkyl haloformates or alcohol esters of haloformic acid utilizable in the condensation reaction, therefore, include the bromo-, chloro, and iodoformates of such typical alcohols as octanol (including the n- and iso-octyl alcohols, undecanol, decanol (lauryl alcohol), dodecanol, pentadecanol, octadecanol, eicosanol and pentaeicosanol. Among the compounds of the above series which are particularly preferred because of their ready availability and relative cheapness are the chloro-substituted formic acid esters, such as octylchloroformate (also called octyl-chlorocarbonate), n-dodecylchloroformate, pentadecylchloroformate, and homologous alkylchloroformates containing from 8 to about 25 carbon atoms per alkoxy group. These reactants may be derived from any suitable source, one method of preparing the chloroformic acid esters being the reaction between carbonylchloride (phosgene) and the corresponding aliphatic alcohol desired for the ester, such as n-octanol, decanol, dodecanol, etc. The higher molecular weight alcohols, such as eicosanol and alcohols containing up to about 25 carbon atoms per molecule may be prepared by hydrolysis of the corresponding olefins or they may be separated from the products formed in the reaction of carbon monoxide and hydrogen.

The reaction between the polyoxyalkylene-substituted amine and the haloformic acid ester may be readily effected by merely heating the amine and the alkyl haloformate, for example, at temperatures of from about 10° to about 120° preferably from about 20° to about 100° C. and may be more efficaciously effected, with resulting greater yield, by heating the reactants in the presence of a basic catalyst or absorbent of the liberated by-product alkyl-halide and/or hydrogen halide. Typical of the substances which promote the condensation reaction are such alkaline compounds as the alkali and alkaline earth metal-oxides, carbonates, hydroxides, mono-basic-oxyhalides, etc. such as sodium and potassium hydroxides, calcium and magnesium carbonates, oxides and hydroxides, barium oxide, barium carbonate, calcium oxychloride, organic bases, such as the tertiary amines, including pyridine, quinoline, tributylamine, etc. and such absorbents as of silica gel or alumina gel particles, activated carbon, etc. One of the preferred procedures, representative of the above described methods for condensing the alkyl haloformate and the polyoxyalkylene-substituted amine reactants, comprises condensing the reactants at a temperature of from about 80° to about 100° C. in the presence of magnesium hydroxide for a reaction period of from about one hour to about six hours and thereafter separating the desired condensation product as a bottoms fraction after distillation of the uncondensed reactants from the reaction mixture.

The species of detergent and surface active agent comprising the compounds of Series (2) herein provided and designated as N-alkyl substituted carbamic acid esters of polyoxyalkylene glycols, in general have the empirical formula:

$$R''-\underset{\displaystyle R'}{\overset{\displaystyle |}{N}}-C-(OR)_xOH$$

wherein R is an alkylene group containing from 2 to about 5 carbon atoms per group, x is a whole number having a value of from 2 to about 25, R′ is a substituent selected from the group consisting of hydrogen, alkyl, and substituted alkyl containing from 1 to about 5 carbon atoms per group, and R″ is a long chain aliphatic alkyl group containing from about 8 to about 25 carbon atoms per group. These products are prepared by the condensation of a long chain mono- or dialkylamine with a chloroformic acid ester of a polyalkylene glycol. Utilizing either mono- or dialkylamines as reactants, these reactants contain one and only one long chain alkyl radical containing from about 8 to about 25 carbon atoms per group and when a dialkylamine is utilized as the reactant, the other alkyl substituents, in addition to the long chain alkyl group, contains not more than about 5 carbon atoms per group. Typical representative mono- and dialkylamines utilizable as reactants in the condensation with the chloroformic acid esters include such compounds as mono-octylamine, amyloctylamine, nonylmethylamine, dodecylmethylamine, octadecylethylamine, eicosanylbutylamine, pentacosanylamine, and others within the general group defined above. As heretofore indicated, the water-solubility of the ultimate product is directly proportional to the chain length of the hydrocarbon radical attached to the carbamic acid portion of the final detergent product and the hydrophobic tendency of such group can only be counterbalanced in the product by the choice of a suitable hydrophilic hydroxy polyoxyalkylene group present in the molecular structure of the carbamic acid ester product. It is evident that the choice of the various substituents in the structure of the present esters to form products hav-

ing optimum surface activity will depend upon the selection of the appropriate hydrophilic polyoxyalkylene group to balance the effect of the hydrophobic long-chain alkyl substituent of the nitrogen atom in the molecular structure of the present esters. When a given detergent product contains a relatively long chain hydrophobic alkyl group, for example, such as an alkyl radical containing from about 10 to about 20 carbon atoms per group, and the product is to be used in aqueous systems, the water-solubilizing capacity of the polyoxyalkylene radical must be correspondingly large and for such purpose, a polyethylene glycol containing a relatively large number of oxyethylene groups per molecule, preferably from about 10 to about 15 per molecule, is utilized to prepare the formate ester. If a higher molecular weight alkylene oxide or polyalkylene glycol is utilized to form the ester, such as a polybutylene glycol, the polyoxyalkylene group must contain a relatively larger number of such oxyalkylene units per molecule, for example (from about 15 to about 25 per molecule) to produce a water-soluble detergent product. The converse is generally true for the preparation of a product designed for use in non-aqueous or organic solvents.

The preparation of the intermediate chloroformate ester of the polyalkylene glycol is effected by reacting the desired polyalkylene glycol in which the alkylene group contains from 2 to about 5 carbon atoms per group with carbonyl chloride (phosgene), utilizing about equimolar proportions of glycol and carbonyl chloride. The polyalkylene glycol ester may also be formed in situ by reacting carbonyl chloride with an alkylene oxide containing from 2 to 5 carbon atoms per alkylene group in a molecular ratio of the reactants which will form the ester of the desired molecular weight containing a sufficient number of polyoxyalkylene groups per molecule required for the product to have detergency. When utilizing the alkylene oxide condensation to form the ester, the molecular ratio of alkylene oxide to carbonyl chloride is determined by the number of oxyalkylene units desired in the final product, and may vary from 2 to about 25 molecular ratios of the respective reactants. When utilizing a polyalkylene glycol, normally in liquid condition, the carbonyl chloride may be merely bubbled into the liquid glycol at a temperature of from about 10° to about 60° C. until a mole of carbonyl chloride per mole of polyalkylene glycol (based on the average molecular weight of the glycols contained in the mixture subjected to reaction) have undergone reaction. When the ester is prepared by reaction of an alkylene oxide, such as ethylene oxide, with carbonylchloride, the reaction proceeds at temperatures of from about 10° to about 100° C., preferably from about 20° to about 50° C., and may be effected at superatmospheric pressures, if desired, to provide essentially liquid phase conditions. In the latter type of reaction, the alkylene oxide is continuously led into the reaction mixture as the condensation proceeds until the resulting halogen-substituted formic acid ester of the corresponding polyalkylene glycol contains the desired number of oxyalkylene groups per molecule, within the range of from 2 to about 25 per molecule. The reaction may also be conducted continuously by feeding the alkylene oxide into a tower packed with a suitable solid packing material, such as berl saddles, silica gel particles, stainless steel rings, etc., while the carbonylchloride reactant is fed into the opposite end of the reactor, the flow rates of the respective reactants being adjusted to provide the proper residence time of the ester in the packed reactor as the alkylene oxide condenses with the free hydroxyl group of the ester chain and continues to add to the end of the polyoxyalkylene glycol portion of the ester.

The condensation of the halogen-substituted formic acid ester of the polyalkylene glycol and the long chain mono- or dialkylamine to form the corresponding N-alkyl-substituted carbamic acid ester of the polyalkylene glycol may be accomplished at reaction conditions essentially similar to the reaction conditions maintained in the condensation of the alkylhaloformate with the polyoxyalkyleneamine, as hereinabove described. Thus, the condensation reaction proceeds at temperatures of from about 10° to about 150° C. preferably from about 20° to about 80° C., and the condensation is further promoted by the presence of an alkaline or basic substance or an absorbent for the hydrogen halide liberated during the condensation reaction. As heretofore indicated, such alkaline substances are preferably selected from the alkali and alkaline earth metal oxides, carbonates, and hydroxides, the organic tertiary amines, and suitable absorbents include such porous substances as activated carbon, particles of silica gel, alumina gel particles, etc., the reaction mixture containing the absorbent or alkaline substance being preferably stirred to effect intimate contact between the reactants and alkaline substance or absorbent. Following completion of the reaction, the unconverted reactants, such as the long chain alkylamine and/or the haloformate may be removed from the desired condensation product by distillation and extraction procedures with suitable solvents for the unreacted starting materials or a combination of such procedures may be employed.

The products of the present invention, characterized generally as N-substituted carbamic acid esters of aliphatic alcohols, including both the polyoxyalkylene glycol carbamate species and the polyoxyalkyleneamine carbamate species herein provided are normally liquid products of low melting point, wax-like materials which may be either soluble in aqueous solutions, or alternatively, soluble in organic solvents, depending upon the structure of the respective compounds, as hereinbefore indicated. The compounds are substantially neutral, that is, they have a pH in aqueous solution of about 7, and hence do not irritate the skin of animals, particularly human skin, when utilized as an aqueous detergent. The species of product provided herein are mutually compatible in admixture with each other and may be furthermore combined in admixture with fatty acid soaps or other ionic or non-ionic detergents. The present carbamic acid esters being non-ionic when dissolved in aqueous solution are not affected by alkaline earth metal ions dissolved in water such as calcium and magnesium ions in hard water. Therefore, they do not form a curd or scum when dissolved in such hard waters, as is typical for certain ionic detergents, such as the fatty acid soaps. The water-soluble detergent products of this invention are normally effective in concentrations of from about 0.1 to about 0.5% in aqueous solution, although higher concentrations may be required in deterging operations in which the present detergent is required to emulsify a large quantity of grease or other oleaginous materials.

The present invention is further illustrated with respect to specific embodiments thereof in

the following representative examples, which, however, are not intended to define within strict limits the operable ranges of the variables contemplated herein.

Example I

A product possessing detergent properties and having the structure of an N-alkyl carbamic acid ester of a polyalkylene glycol is prepared by the condensation of a chloroformic acid ester of a polyalkylene glycol (a polyoxyalkylene chloroformate) with an N-alkylamine. The reactants utilized in the condensation reaction are dodecylmethylamine and the polyoxyethylene glycol ester of chloroformic acid in which the polyoxyethylene chain contains an average of about 15 oxyethylene groups per ester radical. The dodecylmethylamine may be prepared in a preliminary reaction by the condensation of sodium methylamide with dodecylchloride at a temperature of from about 20° to about 30° C. in a closed pressure autoclave in which the pressure is increased to about 10 atmospheres with methylamine. In the preparation of the reactants, methylamine in excess is led as a gas into the pressure autoclave containing finely divided particles of sodium which are heated to a temperature of about 80° C. as the reactor is rotated. The mixture is thereafter cooled to a temperature of −30° C. to liquefy the methylamine and thereafter dodecylchloride formed by the hydrochlorination of dodecylene is admitted into the autoclave and the reactor heated to a temperature of about 20° C., which increases to about 30° C. in the ensuing exothermic reaction. The excess methylamine is removed from the reaction heating the autoclave to distill off the low boiling methylamine. The desired dodecylmethylamine in the form of its hydrochloride salt, may be recovered from the reaction mixture by extraction with dilute hydrochloric acid solution.

The polyalkylene glycol ester of chloroformic acid in which the ester contains an average of about 15 polyoxyethylene groups per molecule is prepared by reacting carbonyl chloride with a mixture of polyethylene glycols having an average of about 15 polyoxyethylene groups per molecule. The reaction is effected by bubbling the carbonyl chloride into the glycol maintained at a temperature of about 30° C. The addition of carbonyl chloride is continued as the reaction mixture is rapidly stirred until approximately a molar equivalent of the carbonyl halide has reacted, the molar ratio being based on the average molecular weight of the polyethylene glycols contained in the glycol mixture.

The chloroformic acid ester of the polyethylene glycol is condensed with the above prepared dodecylmethylamine by mixing approximately equimolar proportions of the reactants and heating the mixture with rapid stirring to a temperature of about 80° C., and in the presence of soda-lime which absorbs the liberated hydrogen chloride. The product is a viscous liquid, soluble in water but only slightly soluble in aromatic hydrocarbons, such as benzene. Other compounds containing both longer and shorter chain length alkyl groups attached to the nitrogen atom of the resulting carbamic acid ester product and containing both shorter and longer chain polyoxyethylene groups in the alkoxy group of the formic acid ester radical when tested for detergency in an aqueous solution by the standard Launder-O-Meter procedure, have somewhat lesser detergencies than the above N-dodecyl carbamic acid ester of the polyalkylene glycol containing an average of about 15 polyoxyethylene groups per molecule. As the chain length of the N-alkyl group increases, the products tend to be less soluble in water and more soluble in organic solvents; the opposite tendency in general holds true as the chain length of the polyoxyalkalene group increases. All products in which the N-alkyl group contains at least 8 and not more than about 25 carbon atoms per group and products containing at least 2, up to about 25 alkylene groups per polyoxyalkylene radical of the carbamic acid ester have surface active properties.

Example II

A detergent product having the structure of an N-polyoxyalkylene carbamic acid ester of an aliphatic alcohol is prepared by the condensation of a haloformic acid ester of an aliphatic alcohol with an N-substituted amine in which at least one and not more than two of the substituent groups is a polyoxyalkylene radical and the other N-substituent is an alkyl group.

The polyoxyalkylene-substituted amine reactant may be prepared by the reaction of a secondary amine with an alkylene oxide a condensation reaction conditions. In the present series of compounds, ethylene oxide is utilized in the reaction to form the polyoxyalkylene chain and various secondary amines are utilized in the condensation to compare the effect of the length of the polyoxyalkylene group and the chain length of the alkyl substituents in the structure of the secondary amine on the detergency of the ultimate product. The preparation of the amines is illustrated by the condensation of ethylene oxide with amylmethylamine in which the condensation is continued until an average of approximately 12 oxyethylene groups are present in the polyoxyethylene chain. The condensation is effected by introducing the ethylene oxide into the amine contained in a stirred pressure autoclave until the polyoxyethylene chain contains the desired number of oxyethylene units. The reaction is effected at a temperature of 50° C. and at a pressure of 40 atmospheres in the presence of a small quantity (about 10 grams per 100 grams of reactants) of pyridine. The mixture is stirred as the reaction proceeds and is allowed to continued until about 12 moles of ethylene oxide have condensed to form the polyoxyalkylene, generally within a reaction period of from about 30 minutes. The polyoxyalkylene group may also be introduced into the structure of the amine as a substituent thereof by reacting the amylmethylamine with a polyethylene glycol containing an average of about 12 oxyethylene groups per molecule, the reaction being carried out at a temperature of about 50° C. and is also promoted in the presence of pyridine.

The condensation of the polyoxyethylene-amylmethylamine and ethylchloroformate to form the detersive carbamic acid ester is obtained by heating the reactants in equimolar proportions at a temperature of about 60° C. in the presence of two molar proportions of calcium hydroxide in aqueous suspension. The reaction mixture is thoroughly stirred to obtain an intimate dispersion of the reactants and the lime suspension, thereby obtaining maximum conversion to the desired end product. The product is a viscous liquid which when dissolved in an aqueous solution and shaken foams profusely and has a detergency approximately equivalent to that of a fatty acid soap, such as sodium-laurate.

The product is water-soluble in all useful proportions normally utilized in deterging operations, although the product tends to become less soluble as the number of polyoxyethylene units per molecule decreases or the chain length of the alkyl groups attached to the nitrogen atom of the carbamic acid ester derivative increases in the number of carbon atoms per group and decreases as the number of alkyl substituents on the nitrogen atom increases from 1 to 2. All products containing at least 2 oxyethylene groups per polyoxyethylene substituent on the nitrogen atom of the carbamic acid ester and containing at least 8 but not more than about 25 carbon atoms per alkoxy group of the formic acid ester have surface active properties, some of which are merely wetting agents and others having detersive properties. The solubility of the products in water tends to decrease as the number of carbon atoms in the alkoxy radical increases without a simultaneous increase in the number of oxyethylene groups in the polyoxyethylene chain. Conversely, the solubility of the product in water and its insolubility in organic solvents, such as hydrocarbons, increases as the number of polyoxyethylene units per molecule increases and the number of carbon atoms in the alkoxy group of the carbamic acid ester decreases.

I claim as my invention:

A compound having the empirical structural formula:



wherein Z is selected from the group consisting of $-(OR)_xOH$ and R'' and Z' is selected from the other member of said group, R is an alkylene group containing from 2 to 5 carbon atoms per group, R' is selected from the group consisting of hydrogen and alkyl containing from 1 to about 5 carbon atoms per alkyl, R'' is an aliphatic alkyl group containing from 8 to about 25 carbon atoms per group, and x is a whole number having a value of from 2 to about 25.

JOSEPH A. CHENICEK.

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