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DETERGENT

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The present invention relates to alkaline surface-tension-reducing agents adapted to be used for wetting, penetrating, dye-levelling, washing or deterging, for producing foam and the like purposes and relates to washing, wetting, textile treating and similar operations wherein such surface-active agents are used. More particularly this invention relates to a specific class of basic chemical compounds which are water-soluble N-alkylated alkylene polyamines having properties making them eminently adapted to such uses.

A wide variety of agents of this character are already known. For the most part, these agents are acids or salts of acids. Of the newer agents of this character those acids and salts which have attained greatest commercial success are sulfonic acids and sulfates and their salts such as the alkylated aromatic sulfonic acids and the sulfated alcohols of high molecular weight and their salts, examples of which are isopropyl naphthalene sulfonic acid and the sodium salt of sulfated lauryl alcohol known under the trade name of "Gardinol" or "Duponol." These materials have certain disadvantages and it is one of the objects of this invention to overcome some of these disadvantages. It is among the further objects of this invention to provide improved surface-tension-reducing agents capable of facilitating wetting, penetrating, foaming, dye-levelling and washing operations, which agents are not acids or salts of acids. Another object of the invention is to provide methods of using these improved agents in the most advantageous manner. Additional objects and advantages of the invention will be apparent from the description which follows hereinafter.

This invention is based upon the discovery that certain N-alkylated alkylene polyamines such as N-n-dodecyl diethylene triamine, N-n-tetradecyl diethylene triamine and N-n-hexadecyl triethylene tetramine in the form of the free bases are surface-active agents of unexpectedly high activity whose properties adapt them admirably for use as detergents, wetting agents, foaming agents and dye-levelling agents. These free basic polyamines are alkaline in reaction and form salts with acids. Unlike the alkylated aromatic sulfonic acid and sulfated alcohol type of agents, which are used preferably in substantially neutral salt form, these polyamines exhibit their best surface activity in washing and similar operations in the form of free bases. Because of this characteristic my agents are superior for use in alkaline baths for textile treatments, dye-levelling, producing foam, etc., in which the other agents are not particularly suited for use. Since most textile treatments are preferably conducted in alkaline baths, rather than in acid baths, the polyamines of this invention when used under such alkaline conditions will be operating at a point at which their effectiveness is at a maximum whereas other agents under the same condition would be operating at a point removed from that of their maximum effectiveness. The polyamines of the invention are among the most powerful surface-tension reducing agents known to me. The surface tension at 25° C. of a 0.0078% solution of N-n-hexadecyl triethylene tetramine is 36.6 dynes per centimeter. In wetting tests in alkaline baths and in washing tests they have proved to be superior to other agents that are recognized as excellent. These agents have greater activity as dye-levelling agents, having a greater protective colloid action, as determined by their low Congo Ruby number (4 for one alkylated alkylene polyamine), than any agent known to me (a commercial product, Igepon-T, has a Congo Ruby number of 20). Furthermore, the polyamines are soluble in organic solvents, which property adapts them to uses for which metallic salts of alkylated aromatic sulfonic acids and sulfated alcohols are not suitable. The N-alkylated alkylene polyamines of this invention are remarkably stable to alkalies and exhibit great resistance to the formation of insoluble precipitates with metallic salts. These and other characteristics and advantages of the agents of this invention will be evident from the results disclosed hereinafter. The compounds for use according to the present invention consist of water-soluble N-alkylated alkylene polyamines. By the term "water-soluble" as used herein is to be understood solubility in water corresponding to as low as about 1 part in 10,000 parts of water (0.01%). These compounds when used as herein described are so efficient at such great dilutions that even a low solubility of this order is sufficient to realize

their advantageous benefits. Dodecyl diethylene triamine,

$$C_{12}H_{25}—NH—C_2H_4—NH—C_2H_4—NH_2$$

and hexadecyl triethylene tetramine,

$$C_{16}H_{33}—NH—C_2H_4—NH—C_2H_4NH—C_2H_4—NH_2$$

are typical compounds for use in the invention. In general, the compounds which are suitable are water-soluble alkylene polyamines substituted in one or more of the amino groups by one or more alkyl groups containing 6 or more carbon atoms. Best effects are obtained, however, when the alkylene polyamine contains only one long-chain substituent in only one amino nitrogen atom, and that amino nitrogen atom in which the alkyl group is substituted is a terminal nitrogen atom. The most active agents of the class are those containing from about 8 to 18 carbon atoms, inclusive, in the alkyl group. The alkylene polyamines which are suitable for alkylation to obtain useful agents according to the invention are those having not more than 6 amino groups per molecule, which may be obtained by the reaction of ammonia with dihalogenated ethane or propane having the halogens on different carbon atoms, that is, not more than one halogen on any single carbon atom. Such alkylene polyamines include ethylene diamine and propylene diamine, diethylene triamine, triethylene tetramines, dipropylene triamines, and the like. Only those alkylene polyamines having not more than one amino group attached to any single carbon atom are preferred. Such polyamines may also be obtained by other known methods of synthesis. Furthermore, the compounds may be more complex than those represented, for example, they may be a complex amine such as

$$NH_2—CH_2CH_2—NH—CH_2CH_2CH_2—NH—CH_2CH_2—NH_2$$

resulting from reaction of an excess of ethylene diamine with trimethylene dichloride, or they may be condensation products of polyamines with each other or with further quantities of alkyl dihalides. The formulae of suitable polyamines which may be alkylated to obtain desirable agents for use according to the invention are exemplified by:

Ethylene diamine	$NH_2—CH_2CH_2—NH_2$
Trimethylene diamine	$NH_2—CH_2CH_2CH_2—NH_2$
Propylene diamine	$NH_2—CH_2—CH(NH_2)—CH_3$
Dipropylene triamines	$NH_2—CH_2CH_2CH_2—NH—CH_2CH_2CH_2—NH_2$
	$CH_3—CH(—NH_2)—CH_2—NH—CH_2—CH(NH_2)—CH_3$
	$CH_3—CH(NH_2)—CH_2—NH—CH_2CH_2CH_2—NH_2$
Diethylene triamine	$NH_2—CH_2CH_2—NH—CH_2CH_2—NH_2$

Since the nomenclature of the alkylene polyamines having more than two nitrogen atoms is rather complex, I have as with the dipropylene triamines in the above list, grouped together all the various isomeric compounds as dipropylene triamines, tripropylene tetramines, etc. and refer to them throughout this specification in that manner.

In preparing preferred agents for use in my invention the alkyl groups which are substituted into the alkylene polyamine vary somewhat with the complexity of the alkylene polyamine molecule. The more amino groups in the alkylene polyamine the greater is the number of carbon atoms in the alkyl group that can be used to produce the most desired compounds. This is shown from the following limits which I set out for preferred compounds for use in my invention.

In the case of alkylated ethylene diamines and propylene diamines the alkyl group should contain more than 6 and less than 10 carbon atoms but if the diamine is alkyl-substituted in both amino groups the total number of carbon atoms in the two alkyl groups should be less than 10.

In the case of alkylated diethylene triamines and dipropylene triamines the alkyl group should contain more than 9 and less than 15 carbon atoms but if the triamine is alkyl-substituted in more than one amino group the total number of carbon atoms in the alkyl groups should be less than 15.

In the case of alkylated triethylene tetramines and tripropylene tetramines the alkyl group should contain more than 9 and less than 19 carbon atoms but if the tetramine is alkyl-substituted in more than one amino group the total number of carbon atoms in the alkyl groups should be less than 19.

Within the above approximate ranges the N-alkylated alkylene polyamines possess a desirable combination of properties which make them especially suitable for use according to the invention and the higher limits of carbon atoms in the alkyl groups correspond approximately to the limits of water solubility as defined herein, that is, the compounds are soluble to at least the extent of approximately 0.01% in water. Representative preferred compounds for use within the purview of this invention are accordingly as follows:

Ethylene diamine or propylene diamine derivatives in which one of the nitrogen atoms of the diamine has been substituted by a heptyl or octyl radical. Diethylene triamine and dipropylene triamine derivatives in which one of the nitrogen atoms of the triamine has been substituted by a decyl, undecyl, dodecyl, tridecyl or tetradecyl radical. Triethylene tetramine or tripropylene tetramine derivatives in which one of the nitrogen atoms of the tetramine has been substituted by a decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl or hexadecyl radical. As used herein, the term "nitrogen atom substituted by an alkyl group" is to be understood to mean that one of the hydrogens attached to the nitrogen atom is replaced by an alkyl group, according to the common use of the term "substitution" as applied to aromatic acyclic compounds.

The compounds which are suitable for use according to the present invention are thus N-alkylated alkylene polyamines having a solubility in water greater than approximately 1 part in 10,000 parts of water, consisting of alkylene polyamines having more than 2 and not more than 6 amino groups per molecule, the different amino groups of which are separated from one another by an alkylene radical selected from the group consisting of ethylene and propylene radicals, at least one of the amino nitrogen groups of which

is substituted by an alkyl group having at least 7 carbon atoms.

Examples of specific compounds whose use is contemplated herein are N-octyl ethylene diamine, N-2-ethylhexyl ethylene diamine, N-dodecyl diethylene triamine, N-tetradecyl diethylene triamine, N-hexadecyl triethylene tetramine, N-heptyl trimethylene diamine, N-tetradecyl tripropylene tetramine, etc. Mixtures of such compounds consisting either of compounds derived from the same alkylene polyamine with different alkyl substituents, such as would result on treating ethylene diamine with mixed alkyl dichlorides, or mixtures of varying degrees of alkylation or mixtures containing compounds derived from different alkylene polyamines with the same or different or mixed alkyl substituents are also contemplated for use herein.

Various methods of preparing compounds suitable for use according to this invention are known. A preferred method of preparing the compounds consists in alkylating the alkylene polyamines by means of an alkyl chloride. Long-chain alkyl chlorides may be obtained by treating long-chain alcohols with an agent such as thionyl chloride. Lauryl (dodecyl) chloride, for example, can be obtained by treating with thionyl chloride the lauryl alcohol fraction derived from the hydrogenation of cocoanut fatty acids. Mixtures of alcohols containing alcohols having from 10 to 16 carbon atoms consisting predominantly of even-numbered carbon-atom alcohols may be used for obtaining corresponding mixed alkyl chlorides and alkylated alkylene polyamines. These mixed alkylated alkylene polyamines are for some purposes as suitable for use in the invention as the compounds derived from a single isomer or homologue.

The alkyl chlorides can be made by other methods, for example, by means of the reaction of alcohols with dry hydrogen chloride using zinc chloride as a catalyst.

The alkylene polyamine is alkylated by heating with the alkyl chloride even without pressure; superatmospheric pressure and elevated temperatures may be used advantageously. The extent to which alkylation is conducted determines the relative amounts of mono- and poly-alkyl substitution. The mono-alkyl alkylene polyamine may be obtained in pure form by fractional distillation.

An example of a method of preparing a typical compound of the invention, N-n-hexadecyl triethylene tetramine,

$$NH_2–C_2H_4–NH–C_2H_4–NH–C_2H_4–NH–C_{16}H_{33}$$

follows: A fraction of alkyl chlorides (boiling at 150° to 160° C. at a pressure of 2 to 3 mm.) obtained by reaction with thionyl chloride of the fraction of alcohols derived from the hydrogenation of cocoanut fatty acids having a boiling point of 180° to 185° C. at a pressure of 15 mm. was used. This fraction of the alcohols corresponded approximately to hexadecyl alcohol and the alkyl chloride formed was substantially pure n-hexadecyl chloride. One mol of this hexadecyl chloride was heated at about 150° C. with about five mols of triethylene tetramine for about 5 hours. The reaction mixture, on cooling, separates into two layers. The upper layer contains the desired reaction product and is distilled under vacuum to separate the unreacted triethylene tetramine. The resulting hexadecyl triethylene tetramine was purified by distillation under vacuum. Its boiling point is approximately 230° to 250° C. at a pressure of 2 to 3 mm. and it is a viscous oil which dissolves in water with a most persistent foam.

In a similar manner other N-alkylated alkylene polyamines may be prepared from corresponding alkylene polyamines and alkyl chlorides. The boiling points of several of these substantially pure N-alkylated alkylene polyamines prepared in this manner are as follows (properties of other compounds of the series are described hereinafter):

	Boiling point
N-n-octyl ethylene diamine	118°–121° C./10 mm.
N-2-ethylhexyl ethylene diamine	108°–110° C./12 mm.
N-n-decyl ethylene diamine	140°–145° C./9 mm.
N-n-tetradecyl ethylene diamine	187°–191° C./9 mm.
N,N'-di-(n-butyl) ethylene diamine	110°–115° C./15 mm.
N-n-dodecyl diethylene triamine	204°–206° C./8 mm.
N-n-tetradecyl diethylene triamine	190°–197° C./2 mm.

Examples of methods of using the compounds according to the invention together with comparative results with similar products follow hereinbelow. The comparative commercial products used in the tests were as follows:

Santomerse D and Santomerse No. 3, which are sodium salts of alkylated aryl sulfonic acids marketed as wetting agents and detergents, respectively.

Aresket, Areskap and Aresklene, which are sodium salts of alkylated diphenyl or phenyl phenol sulfonic acids.

Gardinol-WA, which is a composition containing the sodium salt of sulfated higher molecular weight alcohols and inorganic salts.

Igepon-T, which is the product resulting from the condensation of oleic acid chloride with 2-chloroethylamine and subsequent treatment with sodium sulphite. Its formula is presumably $C_{17}H_{33}CO—NH—CH_2CH_2SO_3Na$.

The alkylated alkylene polyamines used in these tests included N-n-decyl ethylene diamine, N-n-dodecyl diethylene triamine, N-n-tetradecyl diethylene triamine, N-n-hexadecyl triethylene tetramine, and a mixed decyl to tetradecyl diethylene triamine (called decyl-tetradecyl diethylene triamine hereinafter (synthesized from the commercial mixture of alcohols derived from cocoanut fatty acids known as "Lorol." In general, Santomerse D and Santomerse No. 3, Aresket, Areskap, Aresklene and the alkylated polyalkylene polyamine exhibit approximately the same stability to acid and alkali. However, the alkylated alkylene polyamines are more stable in hard water and are more stable to the formation of insoluble precipitates with metallic salts.

Whereas the sulfonated and sulfated products are in general insoluble in organic solvents, with the exception of alcohols, the alkylated alkylene polyamines are soluble in alcohols, carbon tetrachloride, ortho-dichlorobenzene, benzene, xylene, kerosene, raw linseed oil, cottonseed oil, turpentine, pine oil, and Carbitol (diethylene glycol monoethyl ether) to the extent of at least 4 parts per 100 parts of the solvent. Because of this solubility and their wetting and cleansing ac-

tion the alkylated alkylene polyamines enhance the effectiveness of organic dry-cleaning fluids which are used for the purpose of cleaning garments and textiles.

Surface tension reduction

In the following table are given the surface tensions in dynes per centimeter of solutions of the indicated concentrations of the various agents in distilled water at 25° C., as determined by the Du Nouy precision-type tensiometer. The surface tension of water is about 72.8 dynes per centimeter at this temperature. A reduction of the surface tension of water to 30 dynes in 0.5% solution is considered excellent and if this reduction is maintained practically unchanged to a dilution as low as that of a 0.03% solution the material is an extremely active surface-tension reducing agent.

Surface tension at 25° C. (dynes per centimeter)

Compound	0.5%	0.25%	0.125%	0.0625%	0.03125%	0.0156%	0.0078%	0.0039%
Dodecyl diethylene triamine	30.3	30.3	30.3					
n-Hexadecyl triethylene tetramine	33.7	33.6	33.7	33.9	34.0	34.7	36.6	
Decyl-tetradecyl diethylene triamine	31.0	31.1	31.0	31.1	31.3	31.6	30.7	38.2
Santomerse D	37.4	37.7	38.3	43.8	47.9			
Santomerse No. 3	34.0	33.5	34.0	32.9	31.7			
Aresket		31.8	33.7	35.6				
Areskap		31.2	31.9		34.7			
Aresklene		32.4	36.6					

The surface tensions of aqueous solutions containing 0.5% of the decyl-tetradecyl diethylene triamine, one of which contains 2% of sulfuric acid and the other of which contains 2% hydrochloric acid, at the same temperature (25° C.) and under the same conditions are 42.3 and 41.8 dynes per centimeter, respectively.

Draves wetting test

The use of wetting agents in baths for textile treatments prior to spinning and for similar operations such as desizing and facilitating penetration of dyes is a well-developed art. In preparing such baths with the compounds of the invention a suitable proportion of the wetting agent is added to give a desired wetting power. From the comparative results given hereinbelow the effectiveness of the various agents at various concentrations for use in such baths are indicated and the concentrations of the alkylated alkylene polyamines to use to obtain desired wetting or penetrating powers can be estimated. The values are represented as seconds required to wet a standard cotton yarn, according to the method of the Draves Wetting Test as set out in the 1937 yearbook of the American Association of Textile Chemists and Colorists. Values ranging from instantaneous in 0.5% solution to 20 seconds in 0.0625% solution are considered excellent. The alkylated alkylene polyamines are especially effective when used alone or in the presence of added alkali and all the values given below represent the results obtained with aqueous solution of the indicated concentrations containing in addition 2% of sodium hydroxide.

	0.5%	0.25%	0.125%	0.0625%	0.03125%	0.0156%
Decyl-tetradecyl diethylene triamine	12.9	9.1	14.6	30.6	75.5	180+
Decyl diethyl triamine	5.5	5.7	9.2	23.4	74.0	180+
n-Hexadecyl triethylene tetramine	12.5	14.7	26.1	42.5	88.0	180+
Santomerse D	2.0	4.0	9.0	32.0	180+	
Santomerse No. 3	5.7	11.1	28.0	93.0	180+	
Aresket	12.0	35.0	85.0	180+		
Areskap	180+					
Aresklene	100.0.	180+				

Dye-levelling and Congo Ruby Number

Another important class of uses of these compounds is as assistants in the preparation and application of dyestuffs. They may be used in the preparation of dyestuffs in readily dispersible form and for the production of inorganic pigments or pigments of azo, basic, acid, vat, and sulfur dyes in a finely divided condition. As penetrants and wetting agents they assist in producing level dyeings, particularly in alkaline dyeing baths. They facilitate dyeing with developed dyes, the dyeing of animal fibers with vat dyes, the dyeing of cellulose acetate fibers with insoluble dyes, dyeing and printing with aniline black, and the dyeing of leather. In printing pastes they assist in the dispersion of the dye or dye component and facilitate its penetration into the natural or synthetic fiber.

The compounds enable the fibrous materials to be wetted very rapidly and make it unnecessary to apply any special boiling operation to the goods before introducing them into the dye bath. Very uniform dyeing is produced even with dyestuffs which make this very difficult when dyed in the usual way. The compounds may be used in a preliminary wetting bath or they may be added directly to the dye bath.

As a measure of the protective colloid action of the compounds, which permits a comparison of the power of various compounds to level dyes on fabrics, prevent a rapid "take" of the dye and thereby permit the dye to enter the interstices of the fiber more thoroughly, the gold number or the Congo Ruby Number are suitable tests. The latter is generally considered to be a better index of the actual action of the materials in dye baths and is described in "Colloid Chemistry" by Jerome Alexander, vol. IV, page 654 (Chemical Catalog Co., New York, 1932) and consists in brief in preparing a 0.01% solution of Congo Ruby dye solution. To 10 cc. of this solution is added 1 cc. of a 2% solution of the protective colloid. The mixture is permitted to stand a definite period of time and then increments of a

10% sodium chloride solution are added, again permitting the mixture to stand a definite period after the addition of each increment. The points at which the color of the dye begins to turn from red to blue are recorded. A change in color of the dye as a result of the addition of the electrolyte indicates a change in the dye particle size. When a material prevents an increase in size it is considered a protective colloid. Ordinarily, strong protective colloids will have a Congo Ruby Number of 20–25, representing the addition of 1.0 to 1.25 cc. of 10% sodium chloride solution before the color of a solution consisting of 1 cc. of 2% protective colloid solution and 10 cc. of 0.01% Congo Ruby solution changes. The Congo Ruby number is 20 times the number of cc. of 10% sodium chloride solution added. If the Congo Ruby Number is less than this the material is an extremely effective protective colloid.

Comparative Congo Ruby Numbers of the compounds of the invention and of various other materials are as follows:

Decyl-tetradecyl diethylene triamine	Less than 4
Santomerse D	22
Santomerse No. 3	28
Aresket	Greater than 80
Areskap	44
Aresklene	Greater than 80
Gardinol-WA	24
Igepon-T	20

Washing baths and detergent action

The soluble alkylated alkylene polyamines are very effective washing and deterging agents. In comparison with the commercial mixture of salts of sulfated higher alcohols and inorganic salts known as Gardinol-WA, the decyl-tetradecyl diethylene triamine is approximately four times as effective, that is, it may be used at approximately one-fourth the concentration to produce the same washing results. On the basis of actual soil removal the decyl-tetradecyl diethylene triamine removes 120% to 140% more soil than equivalent concentrations of Gardinol-WA under the same conditions, that is, the mixture of sulfated higher alcohol salts is only 70% to 85% as effective. The comparative results with the alkylated alkylene polyamines vary with soft and hard water, the polyamines being superior in soft water but being even more superior in hard water. Results showing the effectiveness of washing in alkaline solutions in which the pH of the wash water has been adjusted are also given. In alkaline solution other compounds are generally less effective than in neutral solution. Results in salt water are also shown.

The washing efficiency of the various compounds was determined by a Standard soil launderometer test, which briefly consists of the following: To a standard cotton fabric is applied under controlled conditions a standard soil solution. This solution is composed of a suspension of carbon black, vegetable oils and mineral oils in carbon tetrachloride. The fabric is then aged for a predetermined period. The aging of the fabric is important because the soil becomes more difficult to remove as it becomes older. The soiled fabric is then washed in a launderometer and each sample is tested in triplicate at various wash intervals (10, 20, 30 and 40 minutes are suitable). The washed samples removed after the various wash intervals are then dried and the lightening of the fabric is determined, using either a Pulfrich photometer or a Lange photoelectric reflection meter or similar instrument. From the values the relative detergency is then established. In the results which follow the improvement in whiteness is expressed as per cent soil removed, which corresponds to 1/2.25 the improvement in "baryta white units" as determined on the Pulfrich photometer. In the tables are also indicated the height of the suds in inches obtained with the solutions of the various concentrations used. The washing results are given in soft water (containing a hardness of 50 p. p. m.) and in hard water (containing a hardness of 300 p. p. m.)

In using the alkylated alkylene polyamines as detergents, various salts may be used to provide increased lather, clearness of solution and to enhance the detergent action. For this purpose, sodium chloride is an especially good detergent builder when used in the ratio of about 30 parts of sodium chloride to 70 parts of alkylated alkylene polyamines. The polyamines, however, appear to be incompatible with soap and have substantially no effect on the detergency of soap when incorporated therewith. Results of washing tests made with a combination of 30 parts by weight of sodium chloride and 70 parts of decyl-tetradecyl diethylene triamine, which gave a clear colorless solution and lathered excellently, are also given in the tables below.

Tests in 50 p. p. m. soft water

Compound	Concentration in per cent	Suds, inches	Percent soil removed after washes of— 10 min.	20 min.	30 min.	40 min.	Average, per cent
Decyl-tetradecyl diethylene triamine	0.05	2	16	29	40	50	34
	0.10	4	33	47	56	61	49
	0.20	4	38	52	59	61	53
Dodecyl diethylene triamine	0.05	2	16	33	46	55	38
	0.10	4	26	42	53	59	45
	0.20	4	41	53	60	64	55
Dodecyl diethylene triamine, pH adjusted to 11	0.10	2	29	39	45	52	41
n-Hexadecyl triethylene tetramine	0.05	1½	22	36	45	53	39
	0.10	4	26	42	49	54	43
	0.20	4	32	46	51	56	46
Tetradecyl diethylene triamine	0.10	4	29	46	55	60	48
	0.20	4	37	49	56	63	51
Gardinol WA	0.05	⅛	5	9	11	13	9
	0.10	4	9	15	19	26	17
	0.20	4	19	30	38	45	33

Tests in 300 p. p. m. hard water

Compound	Concentration in per cent	Suds, inches	Percent soil removed after washes of—				Average, per cent
			10 min.	20 min.	30 min.	40 min.	
Decyl-tetradecyl triethylene triamine	0.05	1½	17	31	41	48	34
	0.10	4	30	42	50	54	44
	0.20	4	34	46	52	55	47
Dodecyl diethylene triamine	0.05	1½	21	35	45	54	39
	0.10	4	29	42	50	58	45
	0.20	4	37	48	52	57	49
Dodecyl diethylene triamine, pH adjusted to 11	0.10	4	30	31	34	40	34
n-Hexadecyl triethylene tetramine	0.05	1½	29	36	45	51	40
	0.10	4	35	39	48	52	43
	0.20	4	42	48	54	60	51
Tetradecyl diethylene triamine	0.10	4	32	45	51	55	45
	0.20	4	36	43	47	50	44
Gardinol WA	0.05	⅓	7	13	18	23	15
	0.10	4	14	26	34	40	29
	0.20	4	26	38	43	46	38

Tests in salt water (3.5% sodium chloride)

Compound	Concentration in per cent	Suds, inches	Percent soil removal after washes of—				Average, per cent
			10 min.	20 min.	30 min.	40 min.	
Dodecyl diethylene triamine	0.20	Trace	35	42	57	66	50

Tests in hard and soft water with 30 sodium chloride—70 decyl-tetradecyl diethylene triamine

Water	Concentration in per cent	Suds, inches	Percent soil removal after washes of—				Average, per cent
			10 min.	20 min.	30 min.	40 min.	
50 ppm. soft water	0.20	4	22	36	42	46	37
300 ppm. hard water	0.20	4	27	39	42	45	38

Ore flotation and foaming agent

The alkylated alkylene polyamines are effective foaming agents. In the washing tests above are indicated the height of suds or foam which are produced with aqueous solutions of various concentrations. These polyamines when added in small amounts to flotation baths will assist in the selective separation of ore constituents. The polyamines themselves, being frothing agents, may be used in connection with the usual collecting agents known to the art to permit a good commercial separation and recovery of valuable ore constituents.

Inasmuch as the above specification comprises preferred embodiments of the invention it is to be understood that the invention is not limited thereto and that changes and modifications may be made therein without departing substantially from the invention, which is defined in the appended claims.

I claim:

1. A detergent comprising a water-soluble alkylene polyamine having at least 2 and less than 4 amino groups per molecule, the different amino groups of which are separated from one another by an alkylene radical selected from the group consisting of ethylene and propylene radicals, at least one of the amino groups of said alkylene polyamine being substituted by an alkyl group having at least 7 and not more than 18 carbon atoms.

2. A detergent comprising a water-soluble N-alkylated alkylene polyamine corresponding to the general formula

$$X—NH—R—(NH—R)_n—NH—Y$$

in which R is an alkylene radical selected from the group consisting of ethylene and propylene radicals, n is 0, 1, or 2, and X is selected from the group consisting of hydrogen and lower alkyl radicals and Y is an alkyl radical having at least 7 and not more than 18 carbon atoms

3. A detergent comprising a water-soluble N-alkylated diethylene triamine in which the N-alkyl group contains at least 10 and not more than 16 carbon atoms.

4. A detergent comprising a mixture of water-soluble N-alkylated diethylene triamines, the N-alkyl groups of which contain from 10 to 16 carbon atoms.

5. A detergent comprising a water-soluble N-dodecyl diethylene triamine in which the dodecyl group is attached to a terminal nitrogen atom.

6. A detergent comprising a water-soluble N-tetradecyl diethylene triamine in which the tetradecyl group is attached to a terminal nitrogen atom.

7. A detergent comprising a water-soluble N-hexadecyl diethylene triamine in which the hexadecyl group is attached to a terminal nitrogen atom.

8. The process of washing and cleansing textile fibers, which comprises subjecting said fibrous material to the action of an aqueous solution of a water-soluble N-alkylated alkylene polyamine as defined in claim 14.

9. The process of washing and cleansing textile fibers, which comprises subjecting said fibrous material to the action of an aqueous solution of a water-soluble alkylene polyamine as defined in claim 15.

10. The process of washing and cleansing tex-

tile fibers, which comprises subjecting said fibrous material to the action of an aqueous solution of a water-soluble N-alkylated diethylene triamine in which the N-alkyl group contains at least 10 and not more than 16 carbon atoms.

11. The process of washing and cleansing textile fibers, which comprises subjecting said fibrous material to the action of an aqueous solution of a mixture of water-soluble N-alkylated diethylene triamines, the N-alkyl groups of which contain from 10 to 16 carbon atoms.

12. The process of washing and cleansing textile fibers, which comprises subjecting said fibrous material to the action of an aqueous solution of a water-soluble N-dodecyl diethylene triamine in which the dodecyl group is attached to a terminal nitrogen atom.

13. The process of washing and cleansing textile fibers, which comprisess subjecting said fibrous material to the action of an aqueous solution of a water-soluble N-tetradecyl diethylene triamine in which the tetradecyl group is attached to a terminal nitrogen atom.

14. The process of washing and cleansing textile fibers, which comprises subjecting said fibrous material to the action of an aqueous solution of a water-soluble N-hexadecyl diethylene triamine in which the hexadecyl group is attached to a terminal nitrogen atom.

15. A detergent composition consisting of a mixture of approximately 30 parts by weight of sodium chloride and 70 parts by weight of a water-soluble alkylene polyamine as defined in claim 1, to each 100 parts by weight of composition.

16. A detergent composition consisting of a mixture of approximately 30 parts by weight of sodium chloride and 70 parts by weight of a water-soluble alkylene polyamine as defined in claim 2, to each 100 parts by weight of composition.

17. A detergent composition consisting of a mixture of approximately 30 parts by weight of sodium chloride and 70 parts by weight of a mixture of N-alkylated diethylene triamines, the N-alkyl groups of which contain from 10 to 16 carbon atoms, to each 100 parts by weight of composition.

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