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3,661,945 REACTION PRODUCTS OF CERTAIN CATIONIC COMPOUNDS WITH ANIONIC COMPOUNDS, COMPOSITIONS CONTAINING SAME AND METHODS FOR PREPARING SAME

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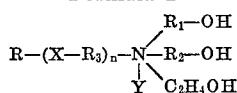
U.S. Cl. 260—401

14 Claims

ABSTRACT OF THE DISCLOSURE

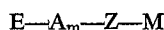
Reaction products of compounds of:

Formula I



and compounds of:

Formula II



BACKGROUND OF THE INVENTION

Organic anionic surface active agents and organic cationic surface active agents have been known to the art. Based upon the experiences of those skilled in the art in the reaction of cationic and anionic organic surface active agents which have been tried, and thereby resulting in the production of water-insoluble precipitates, a general rule has evolved that water-insoluble precipitates would always be produced in such reactions.

CROSS REFERENCE TO RELATED APPLICATION

U.S. Patent application of Hans S. Mannheimer, the applicant herein, Ser. No. 883,268 filed Dec. 8, 1969.

SUMMARY OF THE INVENTION

It was unexpected and surprising to discover that water soluble reaction products and compositions of matter containing same were produced when a particular group of cationic organic surface active agents, namely the quaternary ammonium salts of the Formula I before set forth were reacted in an aqueous system with anionic organic detergent surface active agents of the Formula II before set forth. Among the methods which are employed to carry out the reaction is to provide an aqueous solution of one or a combination of two or more compounds of Formula I and then combine therewith one or a combination of two or more compounds of Formula II which may or may not be in aqueous solution, or one or a combination of two or more of the difficultly soluble compounds of Formula I may be added to water and combined with one or a combination of two or more compounds of Formula II which may or may not be in aqueous solution and heated to and maintained at elevated temperature up to about 100° C. to cause solution of the compounds of Formula I for reaction with compounds of Formula II. Also if desired, even when compounds of Formula I are first in solution before the addition of compounds of Formulas II, such mixtures may be heated to and maintained at elevated temperatures up to 100° C.

In general the reaction products and compositions of this invention are preferably produced by providing an aqueous solution of one or a combination of two or more compounds of Formula I which is combined with an aqueous solution of one or a combination of two or more compounds of Formula II. The ratio by weight of the

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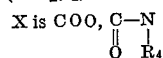
compounds of Formula I to the compounds of Formula II so combined is in the range of about 1–20 to about 1–1 and preferably about 1–15 to 1–4, and the ratio by weight of water to the combined weights of the compounds of Formulas I and II is in the range of about 99.8–2 to about 30–70.

The novel reaction products and compositions of this invention find application as hair conditioners in shampoos and laundry detergents, generally those of the high concentrations are more suitable as hair conditioners and those of the lower concentrations as laundry detergents. They are highly efficient hair and skin conditioners, without reducing foaming as do the more conventional conditioners which for the most part are super-fattening agents. They also find application as components in conventional shampoos, facial cleansers and the like. It is understood, of course, that those of high concentration may be diluted with water to provide the low concentration solutions for laundry detergent uses. Particularly suitable for this purpose are such solutions wherein the ratio of the combined weights of compounds of Formulas I and II employed to water is in the range of about 0.2–99.8 to about 1–99.

In all of the formulas and groups hereinbefore and hereinafter set forth, unless otherwise defined;

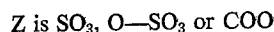
R is a hydrocarbon radical of 8–24 carbon atoms and is alkyl or olefinic; (By the term "olefinic" employed in the present description and claims, I mean an open chain, straight or branch, hydrocarbon radical having 1–4 ethylenic linkages therein).

Each R₁, R₂ and R₃ is an alkylene group of 2–4 carbon atoms:

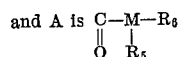


R₄ is hydrogen or alkyl of 1–4 carbon atoms;

E is a hydrocarbon radical of 6–18 carbon atoms and is alkyl or olefinic or alkyl-aryl, with the aryl portion being mononuclear (—C₆H₄—) and the alkyl portion being 6–12 carbon atoms;



when n is zero and Z is SO₃, E is alkyl or alkyl-aryl; when n is zero and Z is O—SO₃, E is alkyl or olefinic; when m is 1 and Z is COO, E is alkyl, olefinic or alkyl-aryl



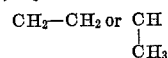
when m is 1 and Z is O—SO₃, E is alkyl, olefinic or alkyl-aryl and A is (O—R₁)_x or



and when m is 1 and Z is SO₃, E is alkyl, olefinic, or alkyl-aryl, A is



R₅ is hydrogen or methyl; when R₅ is methyl, R₆ is CH₂; when R₅ is hydrogen, R₆ is



R₇ is hydrogen, an alkyl radical of 1–4 carbon atoms or an alkylol radical of 2–4 carbon atoms;

M is hydrogen, sodium or potassium or obvious equivalent such ammonium or other monovalent cation;

Y is bromine or chlorine;

n is zero or 1;

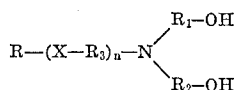
m is zero or 1;

x is 1–12.

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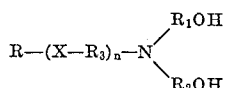
The compounds of Formula I and aqueous solutions thereof may be produced by following the procedures described in my copending U.S. Patent application, Ser. No. 883,268, filed Dec. 8, 1969. That entire application is hereby incorporated herein and by this reference shall have the same force and effect as if it was in its entirety recited herein.

As set forth in my copending application, compounds of the formula



are reacted with ethylene halohydrin ($\text{Y}-\text{C}_2\text{H}_4\text{OH}$) in an amount of water measuring at least 100% of the combined weights of said reactants to produce aqueous solutions of the resultant quaternary ammonium salts of Formula I.

The general method for producing said solutions of compounds of Formula I is to charge the desired amount of water into a reaction vessel equipped with a stirrer and reflux condenser. About 1 mole of a reactant of the formula

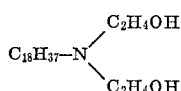


and about 1.1 to 1.5 moles of the halohydrin reactant is then added to the water in amount at least equal to and generally about 1-20 times the combined weights of said reactants. The mass is heated to reflux (boiling under a reflux condenser) at about 105°-110° C. while being constantly stirred over a period of about 8-16 hours or until there is no change in the pH after further refluxing. At the end of that period the reaction is substantially completed and there is obtained a clear about 50-5% solution of the resultant quaternary ammonium salt measuring at least 90 and generally about 95% of theoretical.

The following are illustrative of examples specific compounds of Formula I which may be employed in the practice of this invention and methods for preparing aqueous solutions thereof.

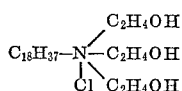
EXAMPLE 1

1450 parts of water, 540 parts (about 1.5 moles) of a reactant of Formula 1:



and 135 parts (about 1.7 moles) of ethylene chlorohydrin are introduced into a glass reaction vessel equipped with a stirrer and a reflux condenser. While being constantly stirred the mass was heated to and maintained in the state of boiling under reflux conditions (105-110° C.) continuously for about 16 hours.

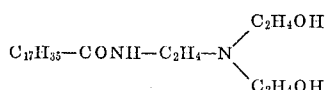
At the end of that period the mass is a clear about 30% aqueous solution, known as Solution 1 and containing approximately 600 parts compound known as Salt 1 and whose formula is:



In this specific example the pH of the solution was 6.3 to 6.7 and further heating did not cause the pH to go below 6.3.

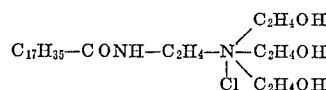
EXAMPLE 2

Use same equipment and method described in Example 1. The reactants are 430 parts (about 1 mole) of a reactant of Formula 2:



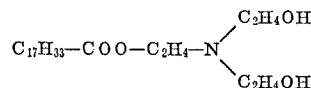
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and 90 parts about (1.1 moles) of ethylene chlorohydrin; and the amount of water is 550 parts. At the end of the 16 hour period of refluxing there is obtained a clear about 50% aqueous solution known as Solution 2 and containing approximately 480 parts of a quaternary ammonium salt known as Salt 2 and of the formula:

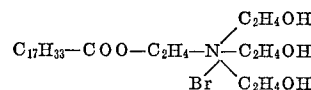


EXAMPLE 3

Use same method and apparatus described in Example 1. The reactants are 415 parts (about 1 mole) of reactant of Formula 3:



and 150 (about 1.2 moles) of ethylene bromhydrin; and the amount of water is 4500 parts. At the end of the 16 hour refluxing period there is obtained a clear about 10% aqueous solution known as Solution 3 and containing approximately 500 parts of quaternary ammonium salt known as Salt 3 and of the formula:



EXAMPLES 4-9

Use same method and apparatus as described in Example 1, but use 3000 grams of water and as reactants 90 grams (about 1.1 gram moles) of ethylene chlorohydrin and instead of the 515 parts of the reactant of Formula 1 use 1 gram mole of respective reactants which are the same as reactants of Formula 1 except that for the radical $\text{C}_{18}\text{H}_{37}$ substitute C_8H_{17} , $\text{C}_{12}\text{H}_{25}$, $\text{C}_{16}\text{H}_{35}$, $\text{C}_{18}\text{H}_{33}$, $\text{C}_{21}\text{H}_{43}$ respectively to obtain four separate clear solutions known as Solutions 4-9 respectively and containing respective compounds which are the same as Salt 1 except that said radicals are respectively substituted for the $\text{C}_{18}\text{H}_{37}$ radical thereof.

EXAMPLES 10-12

Use same method and apparatus as described in Example 2, but use 3000 grams of water and as reactants 90 grams of ethylene chlorohydrin and instead of the 430 parts of the reactant of Formula 2 use 1 gram mole of a reactant of that formula except that $\text{C}_{17}\text{H}_{35}$ radical is substituted by C_9H_{19} , $\text{C}_{11}\text{H}_{23}$, $\text{C}_{17}\text{H}_{31}$ respectively to obtain three separate clear solutions known as respective Solutions 10-12 and containing respective compounds which are the same as Salt 2, except that said radicals are respectively substituted for the $\text{C}_{17}\text{H}_{35}$ thereof.

EXAMPLES 13-16

Use same method and apparatus as described in Example 3, but use 3000 grams of water and as reactants 140 grams (about 1.1 gram moles) of ethylene bromhydrin and instead of the reactant of Formula 3 use 1 gram mole of reactants of that formula except that the $\text{C}_{17}\text{H}_{35}$ radical is substituted by C_9H_{19} , $\text{C}_{17}\text{H}_{31}$, $\text{C}_{11}\text{H}_{23}$ and $\text{C}_{21}\text{H}_{43}$ respectively to obtain four separate clear solutions known as Solutions 13-16 respectively and containing salts known as Salts 13-16 respectively of the same formula as the Salt 3 except that the said radicals are respectively substituted for the $\text{C}_{17}\text{H}_{35}$ therein.

EXAMPLE 17

Use same method and apparatus of and components in amounts given in Example 2, except that for the reactant of Formula 2, use like amount of a compound which differs therefrom only in the substitution of CH_3 for the H of the CONH group to obtain a clear solution known as Solution 17 which is of the same formula as Salt 2

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except that CH_3 is substituted for the H of the CONH group thereof.

EXAMPLE 18-ON

Use same method and apparatus described in Examples 1-17, use 3000 grams of water, 100 grams of ethylene chlorhydrin and instead of the reactants of Formulas 1-17 substitute 1 mole of reactants of the same as Formulas 1-17 except that either one or all of the C_2H_4 groups therein are substituted by $(\text{CH}_2)_3$ or $(\text{CH}_2)_4$ or one C_2H_4 group is substituted by one of said groups and another by the other of said groups to obtain many clear solutions known as Solutions 18-on containing respective salts which differ from salts 1-17 by said substitutions in these other reactants.

Also the same number of moles of ethylene chlorhydrin are substituted for the ethylene bromhydrin in all of the foregoing examples where the latter is used to obtain additional aqueous solutions of the salts which now have Br substituted for Cl. For example, a salt the same as Salt 3 is produced and differs therefrom in the substitution of Cl for the Br. Also the same number of moles of ethylene bromhydrin are substituted for the ethylene chlorhydrin in all of the examples where the latter is used to obtain additional aqueous solutions of the salts which now have Cl substituted for Br. For example, a salt the same as Salt 1 is produced and differs therefrom by the substitution of Br for Cl thereof.

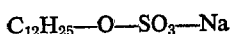
PREFERRED EMBODIMENTS OF THE INVENTION

The following examples are given by way of illustration and not limitation, with all parts being by weight unless otherwise specified.

EXAMPLE 1P

Into a glass vessel were charged 40 parts by weight of a 30% aqueous solution of a compound:

IIa



while said solution was being constantly stirred there were slowly added thereto $3\frac{1}{3}$ parts by weight of Solution 1 (30% concentration of Salt 1) of Example 1. The addition was made at room temperature (about 70°F .) and stirring was continued for a period of about ten minutes after the last increment of Solution 1 was added. At the end of that period the resultant mass contained the reaction product of Salt 1 and IIa in about 30% concentration. The resultant mass was visually examined by the naked eye and found to be crystal clear and is known as Product 1P. A sample of that mass after being allowed to stand over night was so examined and found to be cloudy.

EXAMPLE 2P

The same procedure, components and amounts thereof as set forth in Example 1P were employed except that in this instance the quantity of said Solution 1 was $6\frac{2}{3}$ parts instead of the $3\frac{1}{3}$ parts by weight. Like before at the end of the ten minute period, the resultant mass contained the Salt 1-IIa reaction product and was visually examined by the naked eye and found to be crystal clear and was cloudy after standing over night and is known as Product 2P.

EXAMPLE 3P

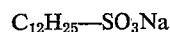
The same procedure, components and amounts thereof as set forth in Example 1P were employed except that in this instance the quantity of said Solution 1 was 10 parts instead of the $3\frac{1}{3}$ parts by weight. Like before at the end of the ten minute period, the resultant mass contained the Salt 1-IIa reaction product and was visually examined by the naked eye and found to be crystal clear and was cloudy after standing over night and is known as Product 3P.

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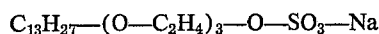
EXAMPLES 4P-33P

Use the same procedure and components and amounts thereof as set forth in respective Examples 1P, 2P and 3P except that instead of using 40 parts of the aqueous solution of IIa, use 40 parts of 30% aqueous solutions respectively of:

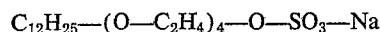
IIb



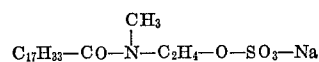
IIc



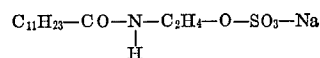
IIId



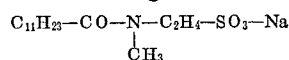
IIe



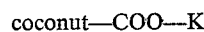
IIIf



IIg

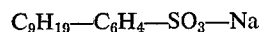


IIh

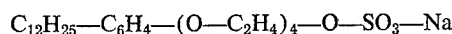


("coconut" represents a mixture of the hydrocarbon radicals in the mixed fatty acids of coconut fatty acid).

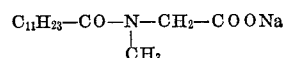
IIIi



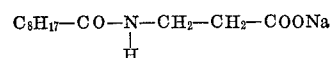
IIj



IIk



III



to provide 30 crystal clear solutions, known as Products 4P-33P respectively.

All of the Products 1P-33P are crystal clear when first made and all of them with the exception of Products 1P-3P remained crystal clear overnight.

EXAMPLE 34P

The same procedure and components and amounts thereof as set forth in Examples 1P-3P were used except that instead of using 40 parts of the aqueous solution of IIa, there was substituted therefor 20 parts of the aqueous solution of IIa together with 20 parts of a 30% aqueous solution of IIb. The resulting mass, known as Product 34P, was crystal clear when first made and so remained overnight.

EXAMPLE 35P

Into a glass vessel were charged 100 parts of water. Then there were added thereto 4 parts of Solution 2 of Example 2, approximately 50% concentration of Salt 2. While the liquid in said vessel was being continuously stirred at room temperature there were slowly added thereto 100 parts of 30% aqueous solution of IIa. After the last increment of IIa solution was added, stirring was continued for an additional period of about 10 minutes. At the end of that period, the resulting mass, known as Product 35P, containing water soluble reaction product of the cationic and anionic employed was crystal clear as viewed by the naked eye and so remained overnight.

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EXAMPLE 36P

Employ same procedure, components and amounts thereof as set forth in Example 35P, except that now 10 parts instead of 4 parts of Solution 2 were used. At the end of the 10 minute period, the resulting mass, known as Product 36P, containing water soluble reaction product of the cationic and anionic employed was crystal clear as viewed by the naked eye and so remained overnight.

EXAMPLE 37P

Employ the same procedure, components and amounts thereof as set forth in Example 35P, except that 14 parts instead of 4 parts of the Solution 2 was used. At the end of the 10 minute period, the resulting mass, known as Product 37P, containing water soluble reaction product of the cationic and anionic employed was crystal clear as viewed by the naked eye and so remained overnight.

EXAMPLES 38P-48P

Employ the same procedure, components and amounts thereof as set forth in the respective three Examples 35P-37P, except that instead of using the 100 parts of the 30% aqueous solution of IIa, use 100 parts of eleven separate 30% aqueous solutions respectively of IIb-III to provide crystal clear solutions, known as Products 38P-48P respectively.

EXAMPLE 49P

Into a glass vessel were charged 10 parts of Solution 3 (about 10% concentration of Salt 3) of Example 3. While being continuously stirred at room temperature, about 70° F., there were slowly added thereto 50 parts of a 30% aqueous solution of IIa. After the last increment of IIa had been added, stirring was continued for a period of about 10 minutes. At the end of that period, the resultant mass, known as Product 49P was visually examined by the naked eye and found to be crystal clear. Product 49P contained the reaction product of the cationic and anionic employed.

EXAMPLE 50P

Employ the same procedure, components and amounts thereof as set forth in Example 49P, except that 20 parts instead of 10 parts of Solution 3 were used. The resultant mass, known as Product 50P was likewise examined and found to be crystal clear.

EXAMPLE 51P

Employ the same procedure, components and amounts thereof as set forth in Example 49P, except that 40 parts instead of 10 parts of Solution 2 were used. The resultant mass, known as Product 51P was likewise examined and found to be crystal clear.

EXAMPLES 52P-82P

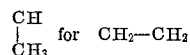
Employ the same procedure, components and amounts thereof as set forth in the three respective Examples 49P-51P, instead of using 50 parts of 30% solution of IIa, use 50 parts of eleven separate 30% aqueous solutions of IIb-III respectively, whereby there were produced 33 more resultant masses, known as Products 52P-82P respectively.

EXAMPLES 83P-ON

Employ the same procedure, components and amounts thereof as set forth in Examples 1P-83P but instead of using Solutions 1, 2 and 3, employ respective solutions of corresponding concentrations of respective salts the same as Salt 1, except that for the C₁₈H₃₇ of Salt 1 substitute respective radicals C₉H₁₉, C₁₂H₂₅ and C₁₇H₃₃, respective salts the same as Salt 2 except that for the C₁₇H₃₅ of Salt 2 substitute respective radicals C₈H₁₇, C₁₁H₂₃, C₁₇H₃₁ and coconut, respective salts the same as Salt 3 except that for the C₁₇H₃₃ thereof substitute re-

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spective radicals, C₈H₁₇, C₁₁H₂₃, C₁₇H₃₁ and coconut and/or instead of using IIa-III substitute respective anionics: the same as IIa except that the C₁₂H₂₅ thereof substitute respective radicals C₁₅H₃₁, C₁₇H₃₃ and coconut, the same as IIb except that for C₁₂H₂₅ substitute respective radicals C₁₈H₃₇ and C₉H₁₉-C₆H₄, the same as IIc except that for C₁₃H₂₇ substitute respective radicals C₉H₁₉ and C₁₂H₂₅ and C₁₈H₃₇, and/or instead of 3 have 1, 2, 4, 5, 6, 7, 8, 9, 10, 11 and 12 O-C₂H₄ groups, the same as Iie and Iig except for the C₁₇H₃₃ and C₁₁H₂₃ groups substitute respective radicals C₁₇H₃₁, C₁₈H₃₇ and coconut, and/or for the CH₃ thereof substitute H and C₂H₄OH respectively, the same as IIh except for coconut substitute respective radicals C₁₁H₂₃, C₁₇H₃₃, C₁₈H₃₇, the same as Iii, except for C₉H₁₉ substitute C₁₁H₂₃, the same as IIj, except substitute C₉H₁₉ for C₁₂H₂₅ and/or instead of 4 have 1, 2, 3, 5, 6, 7, 8, 9, 10, 11 and 12 O-C₂H₄ groups, the same as IIk, except for C₁₁H₂₃ substitute respective radicals C₈H₁₇, C₉H₁₉, C₁₇H₃₃ and coconut, the same as III substitute for C₈H₁₇ respective radical C₉H₁₉, C₁₁H₂₃, C₁₇H₃₃ and coconut and/or substitute



All of these hundreds of different products which may be produced according to this invention contain the reaction products of the cationics and anions employed and upon being produced are crystal clear when visually observed by the naked eye. Such products are solutions of such reaction products which I believe to be in the nature of complexes. All of such products except those produced by the reaction of cationics of Formula I where n is zero with the alkyl sulfates will remain clear upon standing for the conventional period employed in determining the shelf life of aqueous soluble shampoo component in water.

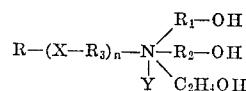
It is to be understood that wherever M is defined in the present description and claims as sodium that this is not by way of limitation for the reason that potassium, hydrogen, ammonium or other monovalent cation may be substituted therefor.

Since certain changes in carrying out the above processes and certain modifications in the compositions which embody the invention may be made without departing from its scope, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

It is also to be understood that the following claims are intended to cover all the generic and specific features of the invention herein described and all statements of the scope of the invention which as a matter of language might be said to fall therebetween, and that they are intended to be inclusive in scope and not exclusive in that, if desired, other materials may be added to my novel composition of matter herein claimed without departing from the spirit of the invention. Particularly it is to be understood that in said claims ingredients or components recited in the singular are intended to include mixtures of said ingredients wherever the sense permits.

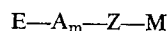
I claim:

1. A water-soluble organic reaction product of a compound of:



and a compound of:

II

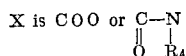


wherein:

R is a hydrocarbon radical of 8-24 carbon atoms and is alkyl or olefinic;

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Each R_1 , R_2 and R_3 is an alkylene group of 2-4 carbon atoms;



R_4 is hydrogen or alkyl or 1-4 carbon atoms;

E is a hydrocarbon radical of 6-18 carbon atoms and is alkyl or olefinic or alkyl-aryl, with the aryl portion being mononuclear and the alkyl portion being 6-12 carbon atoms;

Z is SO_3 , $\text{O}-\text{SO}_3$ or COO ;

when m is zero and Z is SO_3 , E is alkyl or alkyl-aryl;

when m is zero and Z is $\text{O}-\text{SO}_3$, E is alkyl or olefinic;

when m is 1 and Z is COO , E is alkyl, olefinic or alkyl-aryl and A is



when m is 1 and Z is $\text{O}-\text{SO}_3$, E is alkyl, olefinic or alkyl-aryl and A is $(\text{O}-\text{R}_1)_x$ or



and when m is 1 and Z is SO_3 E is alkyl, olefinic, or alkylaryl and A is



R_5 is hydrogen or methyl;

when R_5 is methyl, R_6 is CH_2 ;

when R_5 is hydrogen, R_6 is CH_2-CH_2 or



R_7 is hydrogen, an alkyl radical of 1-4 carbon atoms or an alkylol radical of 2-4 carbon atoms;

M is hydrogen, sodium or potassium or obvious equivalent such ammonium or other monovalent cation;

Y is bromine or chlorine;

n is zero or 1;

m is zero or 1;

x is 1-12.

2. A water soluble organic reaction product according to claim 1;

n is zero;

R_1 and R_2 are C_2H_4 ;

R is $\text{C}_{18}\text{H}_{37}$;

Y is chlorine.

3. A water soluble organic reaction product according to claim 1;

n is 1;



and R_1 , R_2 and R_3 are C_2H_4 ;

R is $\text{C}_{17}\text{H}_{35}$;

Y is chlorine.

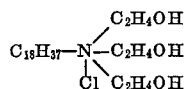
4. A water soluble organic reaction product according to claim 2;

m is zero.

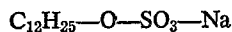
5. A water soluble organic product according to claim 3;

m is 1.

6. A water soluble organic reaction product according to claim 1; I is

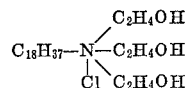


and II is



10

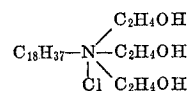
7. A water soluble organic reaction product according to claim 1; I is



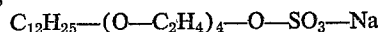
and II is



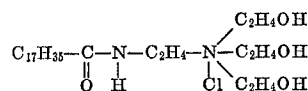
8. A water soluble organic reaction product according to claim 1; I is



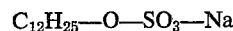
and II is



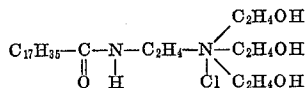
9. A water soluble organic reaction product according to claim 1; I is



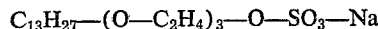
and II is



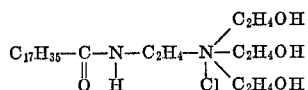
10. A water soluble organic reaction product according to claim 1; I is



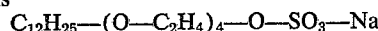
and II is



11. A water soluble organic reaction product according to claim 1; I is



and II is



12. The method comprising reacting in water a cationic compound of Formula I and an anionic compound of Formulas II defined in claim 1.

13. The method according to claim 12; the ratio by weight of the cationic compound to the anionic compound is in the range of about 1-20 to 1-1.

14. The method according to claim 12; the ratio by weight of the cationic compound to the anionic compound is in the range of about 1-15 to 1-4, and the ratio by weight of the water to the combined weights of the anionic and cationic compounds is in the range of about 30-70 to about .2 to 99.8.

References Cited

UNITED STATES PATENTS

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2,993,918	7/1961	Mannheimer et al.	260-401

ELBERT L. ROBERTS, Primary Examiner

U.S. Cl. X.R.

252-152; 424-70

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,661,945

Dated May 9, 1972

Inventor(X) Hans S. Mannheimer

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In each of Lines 43 and 44 of Column 2 "n" is deleted and "m" substituted therefor.

"I" is placed in the middle of Line 63 of Column 8.

Column 9 Line 6 "op", 2nd occurrence should read -- of -- .

Column 9 Line 13 "M" is deleted and "m" substituted therefor.

In the last line of Claim 14 ".2-99.8" is deleted and

"99.8-.2" substituted therefor.

Signed and sealed this 20th day of November 1973.

(SEAL)

Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

RENE D. TEGTMEYER
Acting Commissioner of Patents