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3,472,820

**POLYMERCAPTO CONDENSATION POLYMERS DERIVED FROM MALEIC ANHYDRIDE COPOLYMERS AND AMINOTHIOLS AND THEIR APPLICATION FOR COSMETIC PURPOSES**

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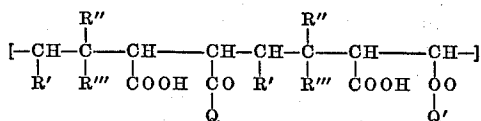
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U.S. Cl. 260-78.5

14 Claims

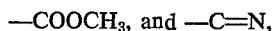
**ABSTRACT OF THE DISCLOSURE**

A polymer that is soluble in aqueous solutions, comprising repeating monomer units having the following formula:

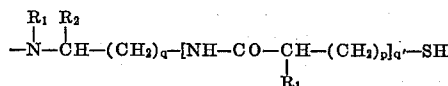


in which:

R' and R'' are both selected from the group consisting of hydrogen, lower alkyl, phenyl, and lower alkoxy, R''' is selected from the group consisting of



Q is a radical having the following formula:



in which:

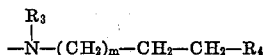
R<sub>1</sub> is selected from the group consisting of H and CH<sub>3</sub>, R<sub>2</sub> is selected from the group consisting of H and COOH,

q is a whole number between 1 and 5, inclusive,

q' is an integer from 0 to 1 inclusive,

p is an integer from 0 to 1 inclusive,

Q' is a radical having the formula:



in which:

R<sub>3</sub> is selected from the group consisting of hydrogen, and lower alkyl,

R<sub>4</sub> is selected from the group consisting of a lower alkyl and a radical having the formula



in which



is selected from the group consisting of lower alkyl amines and a heterocyclic ring,

m is a whole number lying between 2 and 4, inclusive.

There is a well known hair waving process known as "setting" the hair which is carried out without using chemicals and is based principally on the step of drying hair which has first been rolled up on curlers to form it into the desired shape.

It is also well known that hair "set" in this manner retains the desired form only for a relatively short time, and that it is extremely sensitive to humidity, since absorption of water by the hair results in destruction of the "set."

Attempts have been made to overcome this disadvantage by applying to the hair aqueous or water-alcohol solutions of natural or synthetic macromolecules which, after the solvent has evaporated, form a film on the hair.

The essential object of these films is to protect the hair against humidity, but it is also necessary for them to improve, if possible, the sheen, flexibility and manageability of the hair. It is also essential that these films be easily removed from the hair by washing or brushing, without "powdering," i.e. without having the film disintegrate into a multitude of fine particles.

The compositions heretofore utilized for this purpose include vegetable resins, alginates, cellulosic derivatives, polyvinylpyrrolidone, vinyl-pyrrolidone/vinyl acetate copolymers, and vinyl acetate/ethylenic acid copolymers.

All of the compositions heretofore used have inherent disadvantages.

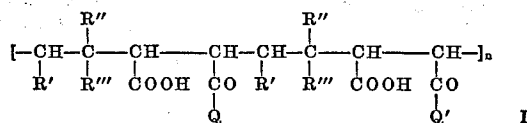
To begin with, they have an insufficient affinity for keratin and do not adhere well to the hair, so that they come off easily when the hair is being combed or brushed, so that such brushing results in the rapid elimination of the wave resulting from the "set."

Moreover, the film is usually hygroscopic, so that the sheen of the hair deteriorates rapidly.

Applicants' assignee has already suggested the use of polymercapto polymers. (See French Patent No. 1,349,140 of Mar. 28, 1962.) These exhibit a notable affinity for keratinic fibers and have cosmetic applications of substantial importance. However, the use of these polymers to set the hair does not produce entirely satisfactory results in that the resulting film on the hair has a crystalline character which leads to "powdering" and leaves the hair dull.

After long research, applicants have discovered new polymers which may be very advantageously used in setting the hair and which at least partially avoid the aforesaid disadvantages, since, on the one hand, they adhere well to the hair and form almost humidity-proof films, and on the other hand, they impart an especially soft and bright appearance to the hair, while rendering it easy to put up.

An object of the present invention is to provide a new article of manufacture which consists of a polymer having —SH groups, alkyl groups and amino alkyl groups in its molecule, characterized by the fact that it has the following formula:



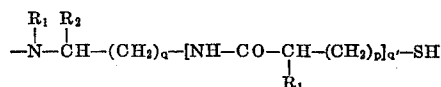
in which:

R' and R'', which may or may not be identical, are selected from the group consisting of a hydrogen atom, a lower alkyl radical, a phenyl radical, and a lower alkoxy radical;

R''' may be a hydrogen atom, the —OCOCH<sub>3</sub> radical, the —COOCH<sub>3</sub> radical, or the —C≡N radical;

n is a whole number;

Q is a radical having the following formula:



in which:

R<sub>1</sub> represents H or CH<sub>3</sub>  
R<sub>2</sub> represents H or COOH



vided with an agitator, a thermometer, a tube for supplying nitrogen, and dropping funnel.

13.3 g. ( $\frac{1}{3}$  mol.) of NaOH is then added to liberate the amine. Then, while stirring and cooling the solution, 71.5 g. (0.5 mol.) of the ethylene/maleic anhydride copolymer sold by the Monsanto Chemical Co. as D.X. 840-11 is then added, the ratio of ethylene to maleic anhydride being 1:088. The specific viscosity of the copolymer at 25° C., has been brought to 0.1 at a concentration of 1% when in solution in dimethylformamide.

After having introduced the polymer into the receiver, 20 g. (0.5 mol.) of NaOH is added to the reaction mixture in small tablets. Then 71.5 g. of the ethylene/maleic anhydride copolymer is added, followed by 20 g. of NaOH tablets in small portions.

At the end of 3 or 4 hours the reaction is terminated and the desired product is isolated by acidification, salted out by means of sodium chloride.

This yields 235 g. of the desired copolymer which appears in the form of a powder which is soluble in water at a neutral or alkaline pH. This represents a yield of about 80 to 85%.

It should be noted that in the final product the tertiary amine function is present in the form of the hydrochloride and that the product contains about 12.5% of sodium chloride, as determined by an analysis of the chloride ion content.

The product is then purified by dissolving it in a mixture of dimethyl formamide and alcohol, the insoluble sodium chloride being eliminated by filtration. The desired product is precipitated from the filtrant by adding ether.

The following analyses have been made:

(a) Of the unpurified product—Calculated: Cl<sup>-</sup>, 8.45% (theoretical hydrochloride content); —SH, 3.34% (taking into account the sodium chloride present). Found: Cl<sup>-</sup>, 16%; —SH, free 2.7%; total 3.3%.

(b) Of the purified product—Calculated: Cl<sup>-</sup>, 8.45%; —SH, 3.78% (taking into account the sodium chloride present). Found: Cl<sup>-</sup>, 9.15% (there was a 1.15% residue of sodium chloride); —SH, free 2.10%; total 2.76%.

The expression "Total —SH" is used to indicate the sum of the free —SH groups in the product and the —SH groups which could be separated from the oxidized (—S—S—) portion of the product by total reduction during the analysis.

Example 2.—Condensation of cysteine and the N,N-diethylpropylene diamine on an ethylene/maleic anhydride copolymer

This is effectuated under the same conditions as those described in Example 1, except that an equivalent quantity of cysteine is substituted for the  $\beta$ -mercapto ethylamine. This yields 47% by weight of a gum which, after purification by dissolving it in dimethyl formamide and precipitation with ether, appears in the form of a pulverulent mass which is soluble in water at a neutral or alkaline pH.

The resulting product was analyzed, with the following results:

Calculated: Cl<sup>-</sup>, 8.05%; —SH, 3.62%. Found: Cl<sup>-</sup>, 7.6%; —SH, free 1.68%; total 2.96%.

Example 3.—Condensation of N-( $\beta$ -aminoethyl)thioglycolamide and N,N-diethylpropylene diamine on an ethylene/maleic anhydride copolymer

This process is carried out under the same conditions as those described in connection with Example 1, except that the  $\beta$ -mercapto ethylamine is replaced by an equivalent quantity of N-( $\beta$ -aminoethyl)thioglycolamide.

After vacuum drying the process yields about 80% by weight of the desired product in the form of a powder soluble in water at a neutral or alkaline pH.

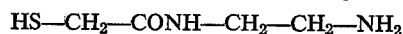
The following analysis of the end product was made:

Calculated: Cl<sup>-</sup>, 7.93%; —SH, 3.13% (taking into account the sodium chloride). Found: Cl<sup>-</sup>, 15% (which

corresponds to 11.7% sodium chloride); —SH, free 2.45%; total 2.6%.

The product thus obtained may be purified by dissolving it in dimethyl formamide and precipitating it with ether.

N-( $\beta$ -aminoethyl)thioglycolamide having the formula:



has been obtained in the following manner:

64 g. (1 mol.) of 96% ethylenediamine is placed in a recipient provided with an agitator, a reflux cooling column, a thermometer, a dropping funnel and a tube for supplying nitrogen. 126 g. (1 mol.) of a 95% solution of ethyl thioglycolate in 100 cc. of absolute alcohol is then introduced drop by drop, while constantly stirring and maintaining the temperature at about 40°-45° C.

When this addition has been completed the solution is heated under reflux for 20 minutes.

The product precipitates on cooling. After draining and drying 107 g. of N-( $\beta$ -aminoethyl)thioglycolamide is obtained, representing a yield of about 80%.

The substance thus obtained is in the form of a white crystalline powder, 99% pure, having a melting point of 133° C.

Example 4.—Condensation of  $\beta$ -mercapto ethylamine and butylamine on an ethylene/maleic anhydride copolymer

This condensation yields about 89% by weight when carried out as described in the foregoing examples, except that the N,N-diethyl-ethylene diamine is replaced by a corresponding quantity of butylamine.

After precipitation in an acid medium, the product is washed with water and, when dried, is a powder soluble in water in an alkaline medium.

It should be noted that, in the present case, the isolated composition is not contaminated with sodium chloride, so that further purification is unnecessary.

The composition obtained has been analyzed as follows:

Calculated: —SH, 4.9%. Found: —SH, free 3.6%; total 4.9%.

Example 5.—Condensation of  $\beta$ -mercapto ethylamine and N-( $\beta$ -aminoethyl)morpholine on an ethylene/maleic anhydride copolymer

The condensation is carried out with a yield of about 65% by proceeding as described in Example 1, except that the N,N-diethyl-ethylene diamine is replaced by an equivalent quantity of N-( $\beta$ -aminoethyl)morpholine.

The product obtained is in the form of a powder which is soluble in water at a neutral or alkaline pH. The powder was analyzed with the following results:

Calculated: Cl<sup>-</sup>, 8.7%; Total —SH, 3.92%; Free —SH, 3.92%. Found: Cl<sup>-</sup>, 11.7% (ClNa, 4.8%); Total —SH, 3.85%; Free —SH, 2.35%.

Example 6.—Condensation of N-( $\beta$ -aminoethyl)thioglycolamide and butylamine on an ethylene/maleic anhydride copolymer

The condensation is carried out with a yield of about 85% by proceeding as described in Example 3, except that the N,N-diethyl-propylene diamine is replaced by an equivalent quantity of butylamine.

The product thus obtained is soluble in water in an alkaline medium, and was analyzed with the following results:

Calculated: Total —SH, 4.65%; Free —SH, 4.65%. Found: Total —SH, 4.55%; Free —SH, 2.52%.

Example 7.—Condensation of  $\beta$ -mercaptoethylamine and N,N-diethyl-propylenediamine on an ethylene/maleic anhydride copolymer

The desired product is obtained with a yield of about 82% by weight by following the same procedure as in Example 1, except that the quantities of amino-thiol and

diamine are altered so that each is equal to 0.5 mol. for a total of 1 mol. of ethylene/maleic anhydride copolymer.

After drying the product obtained is a powder which is soluble in water at a neutral or alkaline pH. This powder has been analyzed with the following results:

Calculated: —SH, 6.28%. Found: —SH, free 4.9%; total 5.5%.

Example 8.—Condensation of  $\beta$ -mercapto ethylamine and N,N-diethyl-propylenediamine on an ethylene/maleic anhydride copolymer

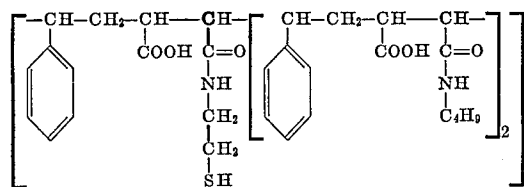
The process is the same as that of Example 1, except that  $\frac{1}{2}$  of a mol. of  $\beta$ -mercapto ethylamine hydrochloride is used for each  $\frac{1}{2}$  mol. of N,N-diethylpropylene diamine.

The product is purified by dissolving it in dimethyl formamide and precipitating it with ether. The composition is obtained in the form of the hydrochloride, with a yield of about 50% by weight. It is soluble in water at a neutral or alkaline pH. The following analysis was made:

Calculated: Cl<sup>+</sup>, 9.7%; —SH, 2.2%. Found: Cl<sup>-</sup>, 8.2%; —SH, free 1.22%; total 1.76%.

Example 9.—Condensation of  $\beta$ -mercapto ethylamine and butylamine on a styrene/maleic anhydride copolymer

The copolymer having the following repeating formula is prepared:



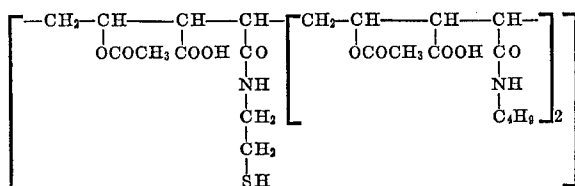
in the same manner as in Example 1, but utilizing: instead of the ethylene/maleic anhydride copolymer an equivalent quantity of the styrene/maleic anhydride copolymer sold under the tradename "Resin SMA 1000 A" by the Texas Butadiene Chemical Corp., and in which the styrene/maleic anhydride ratio is 1:0.86; and instead of N,N-diethyl-propylenediamine, an equivalent quantity of butylamine.

The desired product is isolated in a conventional manner by precipitation in an acid medium. A yield of 93% is obtained and the product is in the form of a powder, an analysis of which gave the following results:

Calculated: Free —SH, 3.88%; Total —SH, 3.88%; N, 4.53%. Found: Free —SH, 1.1%; total —SH, 3.16%; N, 3.95%.

Example 10.—Condensation of  $\beta$ -mercapto-ethyl-amine and n-butyl-amine on a vinyl acetate/maleic anhydride copolymer

A polymercapto condensation copolymer having the following repeating formula is prepared:



by condensing  $\beta$ -mercapto-ethyl-amine and n-butyl-amine on a vinyl acetate/maleic anhydride copolymer, in the following manner:

The starting copolymer is a vinyl acetate/maleic anhydride copolymer obtained in a conventional manner by copolymerizing equimolecular quantities of vinyl acetate and maleic anhydride in toluene in the presence of benzoyl peroxide, which acts as a catalyst.

This copolymer, in a 1% solution in dimethyl formamide, has a specific viscosity of 0.17 at a temperature of 25° C.

The anhydride function has been introduced in a proportion such that the molar ratio between the vinyl acetate and maleic anhydride in this polymer is 0.93/1.

The copolymerization has been so carried out as to produce a copolymer which is water-soluble in a basic medium.

3.89 (0.033 mol.) of the hydrochloride of  $\beta$ -mercapto-ethyl-amine, 4.9 grams (0.066 mol.) of n-butylamine and 100 cm.<sup>3</sup> of water are placed in a vessel provided with an agitator, a thermometer, a tube for introducing nitrogen, and a dropping funnel.

The amine is then liberated from its hydrochloride by adding 3.3 cm.<sup>3</sup> (0.033 mol.) of an aqueous 40% soda solution.

8.9 grams (0.5 mol.) of the vinyl acetate/maleic anhydride copolymer is then added, while stirring and cooling the solution.

5 cm.<sup>3</sup> (0.5 mol.) of an aqueous 40% sodium hydroxide solution is then added to liberate the amine and solidify the carboxyl group of the copolymer.

8.9 grams (0.5 mol.) of the vinyl acetate/maleic anhydride copolymer is then added, together with 5 cm.<sup>3</sup> (0.5 mol.) of an aqueous 40% sodium hydroxide solution.

The reaction is completed in three hours.

The solution is then acidified with hydrochloric acid to precipitate the desired product, which yields 78% by weight, i.e. 19.5 grams of the copolymer according to the invention.

The product is yielded in the form of a white powder which is water soluble at an alkaline pH, and which has the following analysis:

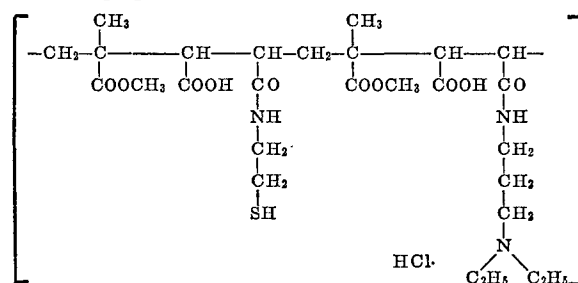
	Percent
SH calculated .....	5.24
SH found .....	2.7

After reducing the oxidized form of the products, a new analysis was made, with the following results:

	Percent
SH calculated .....	5.24
SH found .....	5.3

Example 11.—Condensation of  $\beta$ -mercapto-ethyl-amine and N,N-diethyl-propylene-diamine on a methyl methacrylate/maleic anhydride copolymer

In accordance with the invention a poly mercapto condensation polymer having the following repeating formula is prepared:



by condensing  $\beta$ -mercapto-ethyl-amine and N,N-diethyl-propylenediamine on a methyl methacrylate/maleic anhydride copolymer, in the following manner:

The starting polymer is a methyl methacrylate/maleic anhydride copolymer obtained in a conventional manner by copolymerizing equimolecular quantities of methyl methacrylate and maleic anhydride in toluene in the presence of azo-bis-iso-butronitrile, which acts as a catalyst.

A 1% solution of this polymer in dimethyl-formamide has a specific viscosity of 0.088 at a temperature of 25° C.

The molar ratio between the methyl methacrylate and the maleic anhydride in this polymer is determined by measurement of the anhydride function as equal to 1.52/1.

Under the same conditions as in Example 1  $\beta$ -mercapto-ethyl amine and N,N-diethyl-propylene-diamine are condensed on the methyl methacrylate/maleic anhydride co-

polymer which has been obtained in the manner already described, using 0.5 mol. of aminothiols and 0.5 mol. of diamine per mol. of methyl methacrylate/maleic anhydride copolymer.

After precipitation and purification, a yield of 68% by weight of the desired copolymer is obtained in the form of a white powder which is water soluble at a neutral or alkaline pH.

This powder has been analyzed as follows:

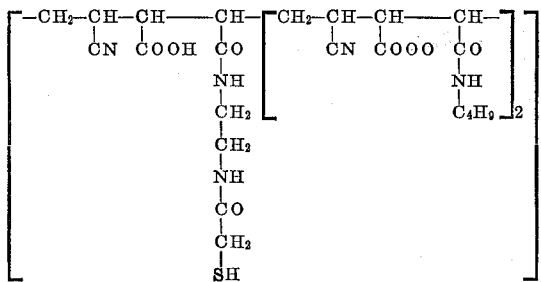
	Percent
SH calculated .....	4.45
SH found .....	2.71

After the oxidized form of the product has been reduced, a new analysis yielded the following results:

	Percent
SH calculated .....	4.45
SH found .....	3.80

Example 12.—Condensation of N-( $\beta$ -amino-ethyl)thioglycolamide and n-butylamine on an acrylonitrile/maleic anhydride copolymer

In accordance with the invention a polymercapto condensation polymer having the following repeating formula is prepared:



by condensing N-( $\beta$ -amino-ethyl)thioglycolamide and n-butylamine on an acrylonitrile/maleic anhydride copolymer, in the following manner.

An acrylonitrile/maleic anhydride copolymer is used as the starting copolymer. This is obtained by copolymerizing equimolecular quantities of acrylonitrile and maleic anhydride in toluene in the presence of benzoyl peroxide, which acts as a catalyst.

The copolymer obtained, when in a 1% solution in dimethyl formamide, has a specific viscosity of 0.055 at a temperature 25° C.

The molar ratio between the acrylonitrile and the maleic anhydride, is determined by measuring the amine function as equal to 1.19/1.

The method is the same as that of Example 10, with the condensation of diamine and aminothiols on this copolymer, except that the  $\beta$ -mercapto-ethyl-amine is replaced by a molecularly equivalent quantity of N-( $\beta$ -aminoethyl)thioglycolamide, and the vinyl acetate is replaced by acrylonitrile.

After the resulting product has been precipitated by means of hydrochloric acid, it is dried, and a yield of 47% by weight of the desired product is obtained.

The product is in the form of a white powder which is water-soluble at an alkaline pH, and has been analyzed with the following results:

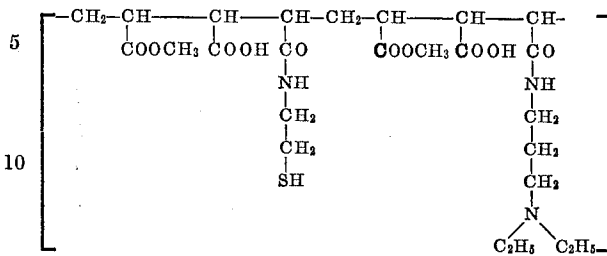
	Percent
SH calculated .....	4.34
SH found .....	2.6

After reduction of the oxidized form of the product, a new analysis yielded the following results:

	Percent
SH calculated .....	4.34
SH found .....	3.5

Example 13.—Condensation of  $\beta$ -mercapto ethamine and N,N-diethyl-propylenediamine on a methyl acrylate/maleic anhydride copolymer

A polymercapto condensation polymer having the following repeating formula is prepared:



by condensing  $\beta$ -mercapto ethylamine and N,N-diethyl-propylene-diamine on a methyl acrylate/maleic anhydride copolymer obtained in a conventional manner by copolymerizing equimolecular quantities of methyl acrylate and maleic anhydride in toluene in the presence of benzoyl peroxide, which acts as a catalyzer.

This copolymer, as a 1% solution in dimethyl-formamide has a specific viscosity of 0.093 at a temperature of 25° C.

The molar ratio between the methyl acrylate and maleic anhydride has been determined by measurement of the anhydride function to be equal to 0.9/1.

By treating the copolymer obtained in this manner in the same way as that described in Example 11, a yield amounting to 70% by weight of a white precipitate is obtained. This precipitate, when dried, appears in the form of a powder which is water-soluble at a neutral or alkaline pH. An analysis of this powder yielded the following results:

	Percent
SH calculated .....	5.25
SH found .....	3.54

After reducing the oxidized form of the product, a new analysis gave the following results:

	Percent
SH calculated .....	5.25
SH found .....	4.27

#### Example 14

Process for producing a hair-setting lotion having the following composition:

Resin resulting from the condensation of $\beta$ -mercapto-ethylamine and N,N-diethylpropylenediamine on the ethylene/anhydride copolymer described in Example 1 .....	g--	3
Ethyl alcohol, q.s.p. ....	degrees--	25
2-amino-2-methyl-1-propanol, q.s.p. ....	pH--	8.5
Tetrasodium salt of ethylene diamine tetracetic acid .....	g--	0.1
Perfume .....	g--	0.2
Water, q.s.p. ....	cc--	100

The resin is first dissolved in 60 cc. of water in the presence of 2-amino-2-methyl-1-propanol until the pH reaches 8.2. The tetrasodium salt of ethylene diamine tetracetic acid is then added to serve as a sequestrant for metals, followed by the mixture of ethyl alcohol and perfume. The volume is then increased to 100 cc. by adding distilled water and, to a pH of 8.5, by adding 2-amino-2-methyl-1-propanol.

20 cc. of this solution is then applied to hair which has been washed and dried, taking care to distribute the solution uniformly over the hair. The hair is then set in a conventional manner. Hair which has been thus treated is lustrous, soft, silky and easily arranged.

The lotion which has just been described materially prolongs the life of the "set" while keeping the air in shape without maning it dull, even in very humid weather.

## 11

## EXAMPLE 15

A setting lotion having the following composition is prepared:

The condensation product of the ethylene/maleic anhydride copolymer and N-( $\beta$ -aminoethyl)thioglycolamide and N,N-diethyl-propylenediamine, obtained as in Example 3	g	2
Ethyl alcohol, q.s.p.	degrees	25
2-amino-2-methyl-1,3-propanediol, q.s.p.	pH	8
Tetrasodium salt of ethylene diamine tetracetic acid	g	0.1
Water, q.s.p.	cc	100

The procedure is the same as that of Example 14. The results obtained are excellent.

## Example 16

A setting lotion having the following composition is prepared:

The condensation product of the ethylene/maleic anhydride copolymer with $\beta$ -mercaptoethylamine and butylamine, obtained as in Example 4	g	2.5
Ethyl alcohol, q.s.p.	degrees	50
Triethanolamine, q.s.p.	pH	7
Tetrasodium salt of ethylene diamine tetracetic acid	g	0.1
Water, q.s.p.	cc	100

The resin is dissolved in 95% ethyl alcohol and triethanolamine is added to facilitate stabilization, followed by the tetrasodium salt of ethylene diamine tetracetic acid. The volume is increased to 100 cc. by adding water and the solution is brought to the desired pH by adding more triethanolamine. This setting lotion yields results comparable to those obtained with the lotions described in the previous examples.

## Example 17

A setting lotion having the following composition is prepared in the same manner as described in connection with Example 16:

Resin resulting from the condensation of $\beta$ -mercaptoethylamine and N,N-diethylpropylenediamine on the ethylene/maleic anhydride copolymer, obtained as in Example 1	g	2.5
Tetrasodium salt of ethylene diamine tetracetic acid	g	0.1
N,N-dimethyl ethanolamine, q.s.p.	pH	8
Ethyl alcohol, q.s.p.	degrees	25
Water, q.s.p.	cc	100

The application of this lotion to the hair yields excellent results.

## Example 18

A setting lotion having the following composition is prepared in the same manner as described in connection with Example 14.

Condensation product of ethylene/maleic anhydride copolymer with $\beta$ -mercaptoethylamine and N,N-diethyl-propylenediamine, obtained as in Example 7	g	2
Vinyl pyrrolidone/vinyl acetate copolymer	g	1
Ethyl alcohol, q.s.p.	degrees	35
2-amino-2-methyl-1-propanol, q.s.p.	pH	9
Perfume	g	0.2
Water, q.s.p.	cc	100

This lotion also gives very satisfactory results.

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## Example 19

An aerosol bomb containing the following ingredients is used to provide an aerosol foam for setting the hair:

Condensation product of ethylene/maleic anhydride copolymer with cysteine and N,N-diethyl-propylene diamine, obtained as in Example 2	g	3
Ethyl alcohol, q.s.p.	degrees	25
2-amino-2-methyl-1-propanol, q.s.p.	pH	8.5
Emulsifying agent (cetyl-stearyl alcohol condensed with 15 mols. of ethylene oxide)	g	2
Perfume	g	0.2
Water, q.s.p.	g	93
Propellant	g	7

The aerosol bomb is made by first solubilizing the resin in 30 cc. of water in the presence of 2-amino-2-methyl-1-propanol. Cetyl-stearyl alcohol (which has first been dissolved in 20 cc. of water, while being slightly heated) is then added, after which the mixture of ethyl alcohol and perfume is added.

The pH is then adjusted to 8.5 by adding the necessary quantity of 2-amino-2-methyl-1-propanol and the weight increased to 93 g. by adding distilled water.

The bomb is completed by adding 7 g. of a conventional propellant such as the fluorinated hydrocarbon sold as "Freon 12."

The product is applied in the form of a very transient foam, which facilitates its uniform distribution throughout the hair, which has previously been washed and dried.

The hair is then set in the usual manner, with excellent results.

## Example 20

In accordance with the invention a setting lotion having the following composition is prepared:

Resin resulting from the condensation of $\beta$ -mercaptoethylamine and n-butyl-amine, on vinyl acetate maleic anhydride copolymer, as in Example 10	g	3
Ethyl alcohol, q.s.p.	degrees	25
2-amino-2-methyl-1-propanol, q.s.p.	pH	8.5
Tetrasodium salt of ethylene diamine tetracetic acid	g	0.1
Perfume	g	0.2
Water, q.s.p.	cc	100

The process is begun by dissolving the resin in 60 cc. of water in the presence of 2-amino-2-methyl-1-propanol to a final pH of 8.2. The tetrasodium salt of ethylene diamine tetracetic acid is added to serve as a sequestrant for metals, followed by the mixture of ethyl alcohol and perfume. The volume is increased to 100 cc. by adding distilled water and the pH adjusted to 8.5 by adding more 2-amino-2-methyl-1-propanol.

20 cc. of the solution obtained in this manner is applied to hair which has been washed and dried, taking care to distribute the solution uniformly. The hair is then set in a conventional manner. Hair treated in this way is bright, soft, silky, vibrant and easily put up.

The lotion which has just been described remarkably prolongs the life of the wave without causing the hair to become dull, even in very humid weather.

## Example 21

In accordance with the invention, a setting lotion having the following composition is prepared:

The condensation product of $\beta$ -mercaptoethylamine and N,N-diethylpropylene-diamine on the methyl methacrylate/maleic anhydride copolymer obtained as in Example 11	g	2
Ethyl alcohol, q.s.p.	degrees	25
2-amino-2-methyl-1,3-propanediol, q.s.p.	pH	8
Tetrasodium salt of ethylene diamine tetracetic acid	g	0.1
Water, q.s.p.	cc	100

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When used as in Example 20, equally good results are obtained.

Example 22

In accordance with the invention an aerosol foam for projection from a bomb to use in setting the hair is prepared from the following constituents:

Condensation product of the acrylonitrile/maleic anhydride copolymer with 1(β-amino-ethyl) thioglycolamide and n-butylamine, obtained as in Example 12	g	3
Ethyl alcohol, q.s.p.	degrees	25
2-amino-2-methyl-1-propanol, q.s.p.	pH	8.5
Emulsifying agent (cetyl stearyl alcohol condensed with 15 mols of ethylene oxide)	g	2
Perfume	g	0.2
Water, q.s.p.	g	93
Propellant	g	7

The aerosol bomb is made by first dissolving the resin in 30 cc. of water in the presence of 2-amino-2-methyl-1-propanol. Cetyl stearyl alcohol which has been dissolved in 20 cc. of water, while heating it slightly, is then added, after which the mixture of ethyl alcohol and perfume is added.

The pH is then brought to 8.5 by adding the necessary quantity of 2-amino-2-methyl-1-propanol and the volume increased to 93 g. by adding distilled water.

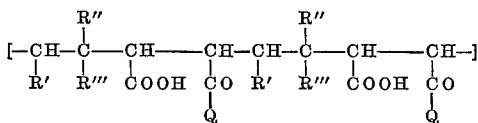
The aerosol bomb is pressurized by adding 7 g. of a conventional propellant such as the fluorinated hydrocarbon sold under the trade name "Freon 12."

The product is applied as a very transient foam, thus facilitating its distribution through the previously washed and dried hair.

The hair is then "set" in a conventional manner, with excellent results.

What is claimed is:

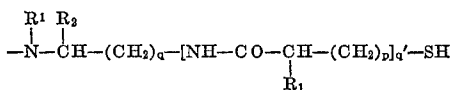
1. a polymer that is soluble in aqueous solutions, comprising repeating monomer units having the following formula:



in which:

R' and R'' are both selected from the group consisting of hydrogen, lower alkyl, phenyl, and lower alkoxy, R''' is selected from the group consisting of —OCOCH<sub>3</sub>, —COOCH<sub>3</sub>, and —C≡N,

Q is a radical having the following formula:

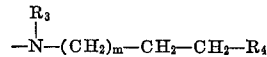


in which:

R<sub>1</sub> is selected from the group consisting of H and CH<sub>3</sub>, R<sub>2</sub> is selected from the group consisting of H and COOH, q is a whole number between 1 and 5, inclusive, q' is an integer from 0 to 1 inclusive, p is an integer from 0 to 1 inclusive,

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Q' is a radical having the formula:



in which:

R<sub>3</sub> is selected from the group consisting of hydrogen, and lower alkyl,

R<sub>4</sub> is selected from the group consisting of a lower alkyl and a radical having the formula



in which



is selected from the group consisting of lower alkyl amines and a heterocyclic ring,

m is a whole number lying between 2 and 4, inclusive.

2. A polymer as claimed in claim 1 in which the substituents Q and Q' constitute from 20 to 80% of the total polymer.

3. A polymer as claimed in claim 1 which is water-soluble at an alkaline pH.

4. A polymer as claimed in claim 1 in which both R' and R'' are hydrogen atoms and R''' is the radical —OCOCH<sub>3</sub>.

5. A polymer as claimed in claim 1 in which both R' and R'' are hydrogen atoms and R''' represents the radical —C≡N.

6. A polymer as claimed in claim 1 in which both R' and R'' are hydrogen atoms and R''' is the radical —COOCH<sub>3</sub>.

7. A polymer as claimed in Claim 1 in which R' is a hydrogen atom, R'' is the —CH<sub>3</sub> radical, and R''' represents the —COOCH<sub>3</sub> radical.

8. The polymer claimed in claim 1 in which Q is β-mercaptoethylamine.

9. The polymer claimed in claim 1 in which Q is cysteine.

10. The polymer claimed in claim 1 in which Q is N-mono methyl mercaptoethylamine.

11. The polymer claimed in claim 1 in which Q is N-(β-aminoethyl)thioglycolamide.

12. The polymer claimed in claim 1 in which Q' is butylamine.

13. The polymer claimed in claim 1 in which Q' is N,N-diethyl-propylenediamine.

14. The polymer claimed in claim 1 in which Q' is N-(β-aminoethyl)morpholine.

References Cited

UNITED STATES PATENTS

2,313,565	3/1943	McDowell et al.	260—78
2,977,334	3/1961	Zopf et al.	260—27

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260—78; 424—47, 72