MICROPALEO

No. 60,1974. RECONSTRUCTION TEST C246K1

OIBAIA. AN. - OR. - FLAMMA. 1978.
CONVENTION APPLICATION FOR A PATENT

X

CONVENION

We hereby apply for the grant of a Patent for an invention entitled:

"WATER-SOLUBLE CATIONIC POLYMER DYE COMPOUNDS,
PROCESS FOR PRODUCING THE SAME AND DYE COMPOSITIONS
CONTAINING THE SAME"

which is described in the accompanying complete specification. This application is a Convention application and is based on the application numbered for a patent or similar protection made in FRANCE on 12th August, 1976.

My address for service is Messrs. Edwd. Waters & Sons, Patent Attorneys, 50 Queen Street, Melbourne, Victoria, Australia.

DATED this 8th day of AUGUST 1977

L'OREAL

By T. A. BARNES

To: THE COMMISSIONER OF PATENTS
In support of the Convention Application made by (hereinafter referred to as the applicant) for a Patent for an invention entitled WATER-SOLUBLE CATIONIC POLYMER DYE COMPOUNDS, PROCESS FOR PRODUCING THE SAME AND DYE COMPOSITIONS CONTAINING THE SAME, do solemnly and sincerely declare as follows:

1. I am authorised by the applicant for the patent to make this declaration on its behalf.

2. The basic application as defined by Section 141 of the Act was made in France on the 12th day of August 1976, by

3. GREGOIRE KALOPISSIS, of 20 Boulevard Bineau, 92200 Neuilly-sur-Seine, France, ALEXANDRE ZYSCHMANN, of 6 rue George Eastmann, 75013, Paris, France, ANDRÉ BUGAUT, of 7 rue des Abondances, 92 Boulogne, France, HENRI SEBAG, of 22 rue Erlanger, 75016 Paris, France, GUY VANLERNBERGHE, of Montjay-La-Tour Commune de Villevaude 77, and JEAN-LOUIS HURON, 5 rue Xavier Massmann, 68100 Mulhouse, France are the actual inventors of the invention and the facts upon which the applicant is entitled to make the application are as follows:

The applicant is the assignee of the said actual inventors.

4. The basic application referred to in paragraph 2 of this Declaration was the first application made in a Convention country in respect of the invention the subject of the application.

DECLARED at Paris, France this 31st day of August 1977.
The dyes are used to dye keratinic fibres.

CLAIMS

1. A dye comprising a water-soluble cationic polymer, having a molecular weight ranging between approximately 800 and 100,000 and having secondary, tertiary or quaternary ammonium amine groups, wherein said amine groups are either part of, or aid in the direct or indirect linking to the polymer chain, an aryl or arylaliphatic chromophore or chromogen group carrying compound, with the proviso that when the main chain of the polymer has amine groups derived from said chromophore or chromogen group carrying compound, the said main chain must also have at least 10% aliphatic amine groups relative to the total number of amine groups of the said chain.
34. A compound of the formula

\[ A-\{ NR - (CH_2)_n \cdot NHCOCH_2Cl \}_p \]

wherein R is alkyl containing from 1 to 3 carbon atoms; p is a whole number between 1 and 3, inclusive; n is a whole number between 1 and 4, inclusive, with the proviso that the values of n for each of the p groups attached to nucleus A can be equal or different; and A represents a substituted or unsubstituted residue of a nitrobenzene dye, an anthraquinone dye, an azo dye, an indamine, an indoaniline, an indophenol, a 1,4-benzoquinone dye or an A-B dye derived from the covalent bonding of compounds A and B which are dyes per se or dye generators of the benzene, anthraquinone or azo series.
The following statement is a full description of this invention, including the best method of performing it known to us:

"WATER-SOLUBLEcation POLYMER DYE COMPOUNDS, PROCESS FOR PRODUCING THE SAME AND DYE COMPOSITIONS CONTAINING THE SAME"
It is known that keratinic fibers are customarily dyed with coloring agents which tend to penetrate the hair. This technique assumes that the dyes used are soluble in the carrier employed and that they have a certain affinity for keratinic fiber. However, these two conditions considerably reduce the number of compounds that can be used for dyeing keratinic fiber. It has also been noted that when some known compounds are used for dyeing hair, they not only have an affinity for keratinic fiber, but also an affinity for the skin, so that dyeing the hair results in a coloration of the scalp and hands of the person applying the dye, which is a disadvantage of this technique.

Heretofore, proposals have been made to use colored polymers for dyeing keratinic fibers, which polymers formed a sheath around the fiber. See, for example, French patents 1,309,399; 1,482,993; 1,484,836; 1,498,461; 1,517,405 and 1,604,203. However, these colored polymers, which are derived from polymers of average or high molecular weight and are only soluble in solvents such as alcohol or a water-alcohol mixture are employed as dye lacquers. These polymers have two disadvantages: first, they are not water-soluble and secondly, they can be eliminated by brushing the keratinic fibers or by shampooing. Thus the coloration of the fibers cannot be considered to be lasting.
The present invention, on the other hand, relates to a new dye which is useful in coloring keratinic fibers, this dye comprising at least one polymer which has a strong affinity for the keratinic fiber to be treated because it contains an aliphatic amine group which facilitates the adsorption of the polymer on said fiber. This polymer is water-soluble and contains a chromophore group which imparts coloration to the polymer. The polymer, which remains outside the keratinic fiber, makes it possible to use a large number of direct dyes for coloring the fibers, these direct dyes not, in themselves, being water-soluble or having any affinity for the keratinic fiber. The new dye according to the present invention has a high degree of resistance to washing with water or detergent compositions and it also resists abrasion very well. Therefore, the dye of the present invention can be used in dye compositions to obtain long-lasting coloring, since the coloring is resistant to shampooing and brushing. However, it is possible to clean the keratinic fibers treated with the polymer substance of the present invention by means of an oxidizing agent, such as a persulphate or $H_2O_2$, or by means of a solvent. Another advantage of the new dye of the present invention is the avoidance of any toxicity problems related to the use of dyes or dye precursors incorporated into the polymer, since the chromophore or chromogen group carriers are not in a free state and are part of the polymer which
remains outside the hair and which, because of its molecular weight, cannot diffuse through the skin. This advantage of the dye according to the present invention is of particular importance in the dyeing of living human hair.

The term "chromophore or chromogen group carrying compound" (CGCC) will be used herein to designate compounds with groups that impart color to them or compounds with groups which, by means of an appropriate transformation, can subsequently impart color to them.

Thus, one object of the present invention is a new dye comprising a water-soluble cationic polymer, having a molecular weight of between approximately 800 and 100,000, and having secondary, tertiary or quaternary ammonium amine groups which either are part of, or aid in the direct or indirect linking to the polymer chain of, an aryl or aryl-aliphatic CGCC, it being understood that if the main chain has amine groups derived from the CGCC, the main chain must also have at least 10% aliphatic amine groups relative to the total number of amine groups of the chain.

It has been noted that according to the present invention, the affinity of certain water-soluble cation resins for keratinic fibers can be used to advantage in obtaining the resistance of the dyes to rinsing and washing as well as a certain number of other advantages described below. Cationic
Polycondensates that can be employed as hair conditioners have already been described, particularly in French patents Nos. 72-42279, 74-27030, 74-39242, 75-15162, 76-20261 and in Luxembourg patents Nos. 73,794 and 73,795.

These cationic polycondensates have a great affinity for hair, an affinity which increases as the hair becomes sensitized by bleaching or permanent waving. It has been noted that if colored compounds or color precursors are grafted onto these cation resins or if these compounds are introduced into the skeleton of said resins, their great affinity for keratinic fiber is still maintained; it being understood that if the main chain has amine groups which are part of the CGCC, it must also have at least 10% aliphatic amine groups relative to the total number of amine groups of the chain.

These aliphatic amine groups make it possible for the polymer to be adsorbed onto the keratinic fiber. Indeed, the keratinic fiber is a negatively charged anion base which cooperates with the cation sites corresponding to the aliphatic amine groups of the polymer according to the present invention.

If the cation polymers of the present invention are derived from cation polymers previously employed as conditioners for the hair, one embodiment of the present invention comprises grafting a colored product, coloring agent or coloring agent precursor onto some of the amine groups of the cationic polymer. However, to maintain the polymer's keratinic fiber adsorption
properties, the amine sites must not all be replaced by the CGCC residues so that the polymer's affinity for keratinic fiber is not eliminated. The CGCC grafted onto the polymer may or may not be water-soluble, since the solubility of the colored cation polymer according to the invention depends on the solubility of the corresponding polymer being grafted with the CGCC residue. In one variant, the polymer of the invention is linear or branched, but not reticulated; in another variant, the polymer may be slightly reticulated, but if it is, the reticulation is limited so that there will be no excessive decrease in the water-solubility of the polymer. The polymers according to the present invention are water soluble. They can be used not only in an aqueous solution, but in a water-solvent medium as well; the solubility subsisting when solvents such as ethanol, alkylene glycols, glycol ethers or similar products are added.

The colored polymers according to the present invention can be obtained by the three processes described below.

In a first process, the dyes according to the present invention can be obtained by reacting reactive colored compounds with cation resins having primary, secondary or tertiary alkylatable amine groups.

In a second process, the dyes according to the present invention can be obtained by reacting colored compounds, having alkylatable phenol or amine groups, with cation resins having reactive groups.
In a third process, the dyes according to the present invention can be obtained by reacting a dialkylatable amino compound or mixture of compounds with other bi-functional derivatives whose functions can react with an amine, one of the two reacting compounds being a CGCC. These functions can, for example, be epoxides, halides or double activated bonds.

In the aforementioned first process, cation resins such as polyamines or polyamino amides can be used, e.g. those described in the French patents Nos. 72-42279, 74-27030 and 74-39242. Commercial resins can also be used, such as polyethyleneimines. All of these resins have primary, secondary or tertiary alkylatable amine groups capable of reacting with reactive CGCCs, especially CGCCs with mobile chlorine or bromine atoms, epoxy groups or double activated bonds.

In a first variation of this first process, the starting reactive molecules that will react with the cation resin have one or several \(-\text{NHCOCH}_2\text{Cl}\) radicals. Preferably, these molecules are compounds resulting from the chloroacetylation of dyes having one or several aromatic amine functions replaced by an aminooalkyl radical or having one or several aminooalkoxy substitutions, it being understood that only the extra-nuclear amine functions are chloroacetylated. These chloroacetylated reactive compounds can belong to various large categories of dyes and can be obtained, for example, by chloroacetylation of nitro benzene dyes, anthraquinone dyes, azo dyes,
indamines, indoanilines, indophenols, 1,4-benzoquinone dyes such as those described in French patent 73-22562 and the dyes described in French patent 1540423.

Representative nitro benzene dyes include reactive dyes obtained by chloroacetylation of ortho-, meta- and para-nitraniline derivatives such as 3-nitro 4-N-β-aminoethylanilino-anisole, Example 4 - British patent 1,159,557 (melting point of the chloroacetylated derivative = 118-119°C); 3-nitro-6-aminophenoxyethylaniline, Example 9 of French patent 74-36651; 3-nitro 4-aminophenoxyethylaniline, Example 13 of French patent 74-36651; 4-nitro N-β-aminoethylaniline (melting point of the chloroacetylated derivative = 142°C); or, by chloroacetylation of nitropara (or meta) phenylenediamine derivatives such as 1-N-β-aminoethylamino-3-nitro-4-N'-methylamino benzene, Example 27 of French patent 1,506,350; 1-N,N-di-β-hydroxyethylanilino-3-nitro-4-N'-β-aminoethylanilino benzene, Example 20 of French patent 1,506,350; 1-methylamino-2-nitro-4-(N'-methyl, N'-β-aminoethyl) amine benzene, Examples 5 and 6 of French patent 1,506,350 (melting point of the chloroacetylated derivative = 140°C); or 1-dimethylamino-3-N-β-aminoethylanilino 4-nitro benzene, Example 5 of French patent 1,506,405 (melting point of the chloroacetylated derivative = 148°C).

Representative anthraquinone chloroacetylated dyes include 1-γ-chloroacetylamino propylamino anthraquinone (melting point = 183°C) obtained by chloroacetylation of 1-γ-aminopropyl
amino anthraquinone, Example 3 of British patent 1,159,557, or 1-γ-chloroacetylaminopropyl amino 4-N-methyl amino anthraquinone (melting point = 215°C) obtained by chloroacetylation of the product described in Example 2 of British patent 1,159,557; or 1-hydroxy-4-γ-chloroacetylaminopropyl amino anthraquinone (melting point = 175°C) obtained by chloroacetylation of the product described in Example 6 of British patent 1,227,825; or 2-β-chloroacetylaminoethyl amino anthraquinone (melting point = 210°C) obtained by chloroacetylation of the product described in Example 7 of British patent 1,159,557. In these examples, the chloroacetylation of the anthraquinone initial reactant is carried out preferably in dioxane in the presence of sodium carbonate. For the first three anthraquinone compounds mentioned above, the amine functions are chloroacetylated as a whole, followed by a selective dealkylation using sulfuric acid. For the fourth anthraquinone compound mentioned above, the extra-nuclear amine function is selectively chloroacetylated.

Representative useful chloroacetylated azo compounds are obtained by coupling diazonium salts with N-ethyl-N-β-chloroacetylaminoethylaniline. As examples, there are the azo compounds of 2-amino benzothiazole and of N-ethyl N-β-chloroacetylaminoethylaniline (melting point = 178°C).

Representative chloroacetylated derivatives of indamines, indoanilines and indophenols include N-[[4-(ethyl β-chloroacetyl- aminoethyl)amino]phenyl] 2,6-dimethyl 3-amino benzoquinone imine
Representative chloroacetylated 1,4-benzoquinone dyes include 2-N-β-hydroxyethyl amino-5-(4-N-ethyl, N-β-chloroacetylaminooethyl amino anilino) 1,4-benzoquinone (melting point = 160 °C) obtained by reacting 4-nitroso N-ethyl, N-β-chloroacetylaminooethyl aniline with 3-β-hydroxyethyl amino 4-methoxy phenol in an ammonia medium in the presence of H₂O₂.

Representative chloroacetylated derivatives of the dyes described in French patent 1,540,423 include N-[(3-nitro-4-β-chloroacetylaminooethyl amino)phenyl] N'-(4'-nitro)phenyl ethylene-diamine resulting from the chloroacetylation of the compound described in Example 17 of French patent 1,540,423; or 1-methylamino-γ-[(2'-nitro-5-N-ethyl N-β-chloroacetylaminooethyl amino)phenyl]-4-aminopropyl amino anthraquinone resulting from chloroacetylation of the compound described in Example 19 of French patent 1,540,423.

The present invention also relates to the new compound of the formula:

$$A-NR - (CH_2)_n - NHCOCH_2Cl \ p$$

wherein R is alkyl having 1 to 3 carbon atoms; p is a whole number between 1 and 3 inclusive; n is a whole number between
l and 4 inclusive, wherein the values of n for each of
the chloroacetylated p groups attached to nucleus A can be
equal or different; and A represents a substituted or non-
substituted residue of a nitrobenzene dye, an anthraquinone
dye, an azo dye, an indamine, an indoaniline, an indophenol,
a 1,4-benzoquinone dye or an A-B dye derived from the
joining through covalence of two compounds A and B which are
dyes, per se, or dye-generators of the benzene, anthraquinone
or azo series.

In a second variation of the first process according
to the present invention, the colored initial reactant has
either one or several aromatic amines replaced by ω-halogenoalkyl,
3-chloro 2-hydroxy propyl or 2,3-epoxy radicals, or halogenoalkoxy
groups on an aromatic nucleus. Representative compounds include
1-β-chloroethylamino-3-nitro-4-N-methyl amino benzene (Example
2 of British patent 1,164,825); 1-N-ethyl N-β-chloroethyl
6-amino-3-nitro 4-N'-methyl amino benzene (Example 3 of British
patent 1,164,825); 1-N-β-bromoethyl amino-3-N'-dimethyl amino-
4-nitro benzene (Example 18 of French patent 1,540,423); (3-
nitro 4-amino) phenyl bromoethyl ether obtained by deacetylation
of (3-nitro-4-acetylamino) phenyl bromoethyl ether described in
Example 15 of French patent 74-36651, 1-(3-chloro2-hydroxy propyl)
amino anthraquinone; or 1-(2,3-epoxy propyl)1-amino anthraquinone.

In a third variation of the first process according to
the present invention, colored reactive compounds can be used
which have chlorotriazinone groups such as in commercial
products known under the tradename "Procion", e.g. those
corresponding to the formulas given in Color Index and
numbered 13245, 13190, 18105 and 18159.

In a fourth variation of the first process according
to the present invention, it is possible to use reactive colored
compounds having a double activated bond, such as the products
known under the tradename "Remazol", for example the vinyl-
sulphones of dyes corresponding to the formulas indicated in
Color Index by references 18852 or 61200.

In the second process according to the present
invention, colored compounds having an alkylatable phenol or
amine group can be used to advantage without appreciably
attenuating the color and in particular, the compounds which
were mentioned for the first and second variations of the first
process (it being understood that these are compounds before
chloroacetylation or halogenoalkylation). As cation resins
having reactive groups, the reaction products of an epihalohydrin
can advantageously be used (epichlorohydrin or epibromohydrin) with
the polyamino-amides resulting from the polycondensation of a
diacid and a polyamide of the type:

$$H_2N-[\text{CH}_2\text{CH}_2\text{NH}_n]-H$$

wherein $n$ has a value of 2 or 3. Representative polyamino-amides
include those disclosed in French patent 74-39:42. When the epihalohydrin is used in proportions of from about 0.8 - 1.3:1 compared to the basic groups, a resin is obtained which may include azetidinium, halohydrin or epoxide groups, all of said groups alkylating amines or phenols and thus making it possible to fix, by covalent bond, colored compounds with an amine or phenol function. The alkylating reactive groups of the resin, which do not react with the colored compounds, can be eliminated by reaction with a nucleophilic compound such as an amine or a mercaptan, for example, or may be maintained in order to increase still further the fixation of the colored polymer onto the substrate to be dyed.

In the third process of the present invention, there can be used colored compounds of the 2-NH₂ type as dialkylatable derivatives in polycondensation reactions with dihalogenated, di-epoxide or di-unsaturated derivatives with double activated bonds. In this case, in addition to colored 2-NH₂ compounds, another bi-secondary derivative is preferably used, for example piperazinc, to increase the water-solubility of the product obtained as well as its affinity for keratinic fibers. It is also possible to use di-halogeno-alkane or di-halohydrin derivatives of colored compounds with secondary or tertiary di-alkylamines. This type of reaction is described in French patent 75-15161.
Representative bifunctional derivatives that can be used to react with the aminated compounds include the derivatives of piperazine such as N,N'-di-(3-chloro-2-hydroxy propyl)-piperazine, N,N'-di-(2,3-epoxy propyl)-piperazine, di-acryloyl-piperazine, diglycidyl ether or ethylene-diamine di-acrylamide; colored di-amino derivatives can also be used with bifunctional derivatives such as those which have just been mentioned, or colored di-halogenated derivatives with di-secondary amines.

For the above first and second processes, the reactions for preparing the halogenated derivatives or react. epoxides are generally carried out in a solvent, with or without the presence of water, at temperatures ranging between 0 and 100°C, but preferably between 30 and 70°C. Solvents that can be used are, in particular, the lower alcohols such as methanol, ethanol, isopropanol, t-butanol, alkoxysthanols, aromatic solvents such as benzene or toluene, or other solvents such as dimethylformamide or acetonitrile. The reactions of the reactive colored compounds with the cation resins are most often carried out in the presence of solvents such as those just mentioned, at temperatures ranging between 30 and 130°C, but preferably between 50 and 90°C. The reaction time generally ranges between about 1 to 10 hours. These reactions can be effected on linear or reticulated cation resins, but it is also possible to crosslink the cationic resins with bifunctional
derivatives after grafting the colored compound. The colored resins are then precipitated in a non-solvent such as acetone, methylethylketone, methylisobutylketone, methyl ether or hydrocarbons such as hexane or heptane. Given the reactivity of the colored compounds which, in addition, are in the presence of a considerable surplus of reactive sites on the resins, and given the possibility of precipitating the colored matter, it is in general relatively easy to purify the colored compounds obtained according to the present invention and, especially, to eliminate those dyes or dye precursors which may not have been condensed on the resin. When the colored material cannot be precipitated, the product obtained can be purified by dialysis after solubilization in water. When colored compounds with amino or phenol groups are made to react with reactive resins, the reactions occur in a solvent or in water. When attempting to conserve the reactive resins, they are acidified with, for example, hydrochloric acid before they are isolated. If, on the contrary, one does not wish to conserve the reactive resins, a nucleophilic compound is added such as an amine or a mercaptan, to consume the normal reactive sites.

The reactions of the third process according to the present invention can be carried out in water, in solvents or in water-solvent mixtures. These reactions occur at temperatures ranging between 50 and 110°C, and preferably between 80 and 130°C.
The reaction time is between approximately 1 and 10 hours.

As indicated previously, the colored compounds according to the present invention have a strong affinity for keratinic substrates. Consequently, they can be used in hair dye compositions. Therefore, another object of the present invention is a dye composition intended for dyeing keratinic material such as hair, wool, fingernails or leather, said composition characterized by the fact that it contains in solution at least one colored polymer as defined above.

An initial advantage of the dye compositions according to the present invention is the possibility of using colored compounds which, normally, do not "ride" on substrates such as hair, wool or leather, by imparting to them an affinity for the substrates by means of the aminated groups of the cationic polymer and by increasing their solubility in the dye composition.

Another advantage of the compositions according to the present invention is the possibility of obtaining a shade which is identical or very similar to that of the CGCC which is grafted to obtain the cationic polymer according to the invention. However, it is also possible to obtain different, lasting shades when different CGCCs are used simultaneously for preparing the same cationic colored polymer according to the invention. In this case, there are no different shades of the same color to be noted for the various color generators present, thus making it possible to obtain a good degree of shade consistency and
stability. Moreover, since the colored polymer according to the present invention behaves as a color heightening retardant on the substrate, there is generally no need to add a stabilizing agent to the compositions of the invention.

When the compounds according to the present invention are used for dyeing keratinic fibers and, in particular, hair, they offer the advantage of being usable in water. Furthermore, the dye compositions according to the invention are shampoo-proof, whether they be non-ionic, cationic or anionic shampoos. Finally, the compositions according to the present invention are advantageous in that they are deposited on the periphery or surface of the fiber, which offers the possibility of a purely surface treatment which does not modify the internal nature of the fiber. In view of the fact that there is no penetration of dye within the fiber, the dye removal operation which precedes a new dyeing operation is facilitated and becomes total; the dye removal is done with oxidizing agents or solvents, as described earlier.

The affinity of the colored polymer for keratinic fibers increases as the fibers become sensitized. However, the compositions according to the present invention have but a very weak affinity for the skin, so that their use results in essentially no coloring of the scalp or hands of the person applying the compositions to the hair.
Moreover, since the molecular weight of the colored polymer of the present invention is several times higher than that of a traditional type dye, diffusion through the skin is considerably reduced, causing almost total disappearance of the toxicity of the colored compounds, dyes or dye precursors which are present within the cationic polymer of the invention. The result is that the compositions of the present invention, which in their free state can be free of dye, are particularly safe with regard to toxicity.

If the colored polymers according to the present invention are prepared by modifying a cationic resin, the resin is generally selected from among resins known for their hair conditioning properties or their fabric finishing properties. It has been noted that in general when there is limited modification of the initial polymer, the colored polymer of the present invention has many of the properties of the original non-colored resin. This means that the compositions of the present invention make it possible to obtain, in addition to coloration of the substrates, effects such as the untangling of fibers, shine, softness and strengthening of the substrate, depending on the effects inherent in the initial cationic resin.

A fundamental characteristic of the dye compositions according to the present invention is the affinity of the cationic polymer of this invention for keratinic substrates such as hair, wool, furs and fingernails, particularly when
these substrates are sensitized. The affinity for the keratinic substrates is mainly a function of the cationic function of the resin, thus, of the percentage of colored compound molecules in relation to the aminated groups of the initial resin. This percentage advantageously ranges between 5 and 100%, and preferably between 10 and 40%. It is noteworthy that the lower this percentage, the more the properties of the colored compound of the invention resemble those of the original cationic resin. In addition, the speed of take up onto the hair increases when the percentage decreases.

The use of the compositions according to the present invention for keratinic fibers imparts to said fibers a certain rigidity and a better hold than that which results when dyeing is done with a traditional-type dye. This result is particularly useful for dyeing hair and for dyeing wool, where a decrease in felting is noted.

The dye compositions according to the present invention can contain one or several water-soluble cationic polymers of the invention. In general, the cationic polymers according to the invention are present in a proportion ranging between 0.01% and 10% and, preferably, between 0.02% and 8% by weight with respect to the total weight of the composition. The pH of the composition is between 1 and 11, and preferably, between 3 and 10. When the compositions according to the invention are used for dyeing hair, the
contact time can vary between 1 and 30 minutes, it being understood that for lotions applied as hair rinses, there is no prolonged contact time, the said lotion being applied, perhaps rinsed and then dried.

In addition to the cationic polymer compounds of the invention, the compositions according to the invention can contain other dyes, particularly azo dyes, anthraquinone dyes, nitrobenzene dyes, 2,5-diaminoquinones, indophenols, indoanilines, indamines, phenylamines and oxidation bases and couplers.

The compositions according to the present invention are provided in the form of an aqueous solution, possibly mixed with alkalizing or acidifying agents and/or solvents and/or polymers and/or cation type treatment products and/or amides and/or thickeners and/or surfactants and/or additives customarily used in hair cosmetics such as sun filters, optical bleaching agents, anti-oxidizing agents, sequesterants and perfumes. The compositions according to the present invention can also contain oxidation agents.

Representative alkalizing agents include mono- or tri-ethanolamine, ammonium hydroxide, sodium phosphate or sodium carbonate. Representative acidifying agents include phosphoric, hydrochloric, lactic, tartaric, acetic or citric acids. These alkalizing or acidifying agents are employed to adjust the pH of the dye compositions to the aforementioned values.
Representative solvents used in the compositions according to the present invention include low molecular weight alcohols having from 2 to 4 carbon atoms, such as ethyl alcohol or isopropyl alcohol or glycols such as ethylene glycol, propylene glycol or butylene glycol, or glycol ethers such as the methyl ether, ethyl ether or butyl ether of ethylene glycol. The aforementioned solvents are present in amounts ranging between 0.5 and 50% by weight and, preferably, between 1 and 15% by weight relative to the total weight of the composition.

The additional polymers contained in the composition according to the present invention can be polymers or copolymers of vinylpyrrolidone, crotonic acid/vinyl acetate, vinylpyrrolidone/vinyl acetate, cationic polymers such as quaternized polyvinylpyrrolidone polymers, quaternized cellulose derivatives, copolymers of N-vinylpyrrolidone/dimethylaminoethyl methacrylate and polyethylene glycol, quaternized by dimethyl sulphate, crosslinked or not.

These additional polymers are employed in concentrations ranging between 0.1 and 3% by weight and, preferably, between 0.3 and 2% by weight, with respect to the total weight of the composition.

The amides contained in the compositions according to the invention may be fatty acid mono- or diethanolamides, oxyethylenated if need be.
The thickeners can be cellulose derivatives such as carboxymethyl cellulose, hydroxypropylmethyl cellulose or hydroxyethyl cellulose.

The surfactants can be anionic, cationic, non-ionic or amphoteric agents such as sulphates, ether-sulphates, fatty alcohol sulphonates, oxyethylated fatty acids or alcohols, oxyethylated alkylphenols, amines and quaternary ammonium salts.

In the compositions according to the invention, the oxidation agents can be $\text{H}_2\text{O}_2$, carbamide peroxide or persalts such as ammonium persulphate. These oxidation agents are present in a proportion ranging between 1 to 6% by weight with respect to the total weight of the composition.

The compositions according to the invention can be in the form of a gel, cream, foaming or milky liquid, and packaged in flasks, tubes or aerosols.

The following non-limiting examples are given to illustrate the present invention. Unless otherwise stated, all parts and percentages are by weight.
Example 1

In 80 cc of a 20:10 mixture of dimethylformamide/methyl "Cellosolve," 13.8 g (basic equivalent, 0.073) of the following polyamino-amide are dissolved, the preparation of which is described in French patent 74-39242:

\[
\begin{align*}
\text{NHCH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{NCOCH}_2
\end{align*}
\]

To this mixture, there are quickly added 12.4 g (0.035 mole) of colored compound of the formula:

\[\text{O} \text{O} \text{NH(CH}_2)_3\text{NHCOCH}_2\text{Cl}\]

dissolved hot in 100 cc of dimethylformamide.

The resulting solution is heated for 4 hours at 70°C, then neutralized with 23 g of sodium methylate in a methanol solution (0.027 mole) and heated again for 2 hours at the same temperature.

The resulting polymer is isolated from its solution by precipitation in 2 liters of acetone. It is a red, powdery solid. Its proportion of condensed colored compound, measured
by spectroscopy, is 34% by weight (wave length of maximum absorption, $\lambda_{\text{max}} = 500$ nm).

Thin layer chromatography is used to verify that the colored polymer no longer contains any detectable amount of initial colored compound.

**Example 2**

In 60 cc of a 20:40 mixture of dimethylformamide/methyl "Cellosolve," 63 g (basic equivalent 0.34) of the following polymer are dissolved, the preparation of which is described in French Patent 74-39 242:

$$\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NHCO(CH}_2)_4\text{CO}$$

To this solution there are added 12 g (0.034 mole) of the chloroacetylated derivative used in Example 1, dissolved in 100 cc of dimethylformamide.

The resulting mixture is heated for 6-1/2 hours, then poured drop by drop into 3 liters of acetone. The resulting polymer precipitates as a gum. It is taken up in a 30:30 DMF/MC mixture, then re-precipitated in the acetone. A soft resin is isolated with a yield of 87%.

Its proportion of condensed colored compound, measured by spectroscopy, is 12.2% by weight ($\lambda_{\text{max}} = 500$ nm).
Example 3

To 30 cc of a 10:20 DMF/MC mixture containing 24.85 g (basic equivalent 0.134) of the resin described in Example 2, 100 cc of DMF solution are added, containing 10 g (0.027 mole) of compound having the formula:

\[
\text{NH(CH}_2)_3\text{NHCOCH}_2\text{Cl}
\]

The resulting mixture is heated for 3-1/2 hours at 60°C, then poured into 3 liters of acetone. A gum is isolated, which is purified by another solubilization and re-precipitation. After drying, a powdery solid is obtained, containing 21.5% by weight of condensed colored compound (\(\lambda_{\text{max}} = 549\) nm), measured by spectroscopy.

Example 4

To 70 cc of a 20:50 DMF/MC mixture containing 33.89 g (0.182 mole) of the resin described in Example 2, 20 g (0.547 mole) of the chloroacetylated derivative used in Example 3 are added, dissolved in 100 cc of DMF.

The mixture is heated for 4 hours at 60°C, then concentrated by partial evaporation of the solvent under reduced pressure. The mixture is poured into 1/2 liter of acetone. The precipitated resin is rinsed several times in acetone.
After drying, a powdery solid is obtained with a yield of 74%, containing 30.5% by weight of condensed colored compound ($\lambda_{\text{max}} = 586$ nm and 549 nm), measured by spectroscopy.

Example 5

To 6 g (basic equivalent 0.0324) of the resin described in Example 2 and dissolved in 10 cc of methyl "Cellosolv" 50 cc of a solution of DMF containing 7.3 g (0.0196 mole) of the chloroacetylated derivative prepared in Example 3 are added. The resulting mixture is then heated for 3 hours at 80°C. Then 1.6 g (0.01 mole) of sodium methylate are added in a methanol solution and heated again for 2 hours at the same temperature. The mixture is then poured into a large excess of acetone.

After drying, a solid is isolated with a yield of 60%, containing 42% of condensed colored compound ($\lambda_{\text{max}} = 548$ nm and 586 nm), measured by spectroscopy.

Example 6

To a solution of 13.86 g (0.0495 mole) of colored compound having the formula:

\[
\text{NH(CH}_2\text{)}_3\text{NH}_2
\]

...
dissolved in 135 g of methyl "Cellosolve", 9.8 g of di(ethylene propyl) piperazine (0.0495 mole) are added. The resulting mixture is then heated for 5 hours at 90°C. The solution is then poured into 1.5 liters of sulfuric ether. A powdery solid is isolated, with an 82% yield, the molecular weight of which is 2960, measured by vapor pressure.

After dialysis, a polymer is isolated with a molecular weight of 3500. It contains 53% by weight of condensed colored compound (λ = 500 nm).

**Example 7**

To 80 g (basic equivalent 0.432) of the resin described in Example 2, in solution in a 150:45 MC/DMF mixture, a solution of 52 g (0.129 mole) of the following colored compound in 500 cc of DMF is added:

![Chemical Structure](image)

The resulting mixture is heated for 5 hours at 70°C, then concentrated by partial evaporation of the solvent under reduced pressure. The concentrated solution is poured into 4 liters of acetone.
After drying, a hard resin is isolated, containing 30% by weight of condensed colored compound (\( \lambda_{\text{max}} = 505 \text{ nm} \)) measured by spectroscopy.

**Example 8**

A mixture of 11.84 g (0.0598 mole) of di-(epoxy propyl)piperazine and 10 g (0.0598 mole) of a colored compound of the formula:

\[
\text{NH}_2 \quad \text{NO}_2 \\
\text{NHCH}_3
\]

in 50 cc of DMF is heated for 13-1/2 hours at 120\(^\circ\)C. The solution is then poured into an extremely large excess of ethanol.

After drying, a powdery solid is isolated, containing 29% by weight of condensed colored compound, measured by spectroscopy.

**Example 9**

A mixture of 19.8 g (0.1 mole) of di-(epoxy propyl) piperazine, 8.35 g (0.05 mole) of a colored compound of the formula:

\[
\text{NH}_2 \quad \text{NO}_2 \\
\text{NHCH}_3
\]
and 4.3 g (0.05 mole) of piperazine in 80 cc of DMF is heated for 12 hours at 120°C. The mixture is then dispersed in 1 liter of acetone.

After drying, a powdery solid is isolated, with a yield of 63%, and containing 11% by weight of condensed colored compound.

Example 10

To 17.6 g (basic equivalent 0.095) of the resin described in Example 2, dissolved in 30 cc of MC, 70 cc of DMF are added, containing 8 g (0.019 mole) of a colored compound of the formula:

\[
\begin{align*}
\text{CH}_2\text{COCHNH}_2\text{CH}_2\text{C} & \\
\text{N} & \\
\text{H}_5\text{C}_2 & \\
\text{N} & \\
\text{Ni} & \\
\text{O} & \\
\text{NiCH}_2\text{CH}_2\text{OH} & \\
\text{CO} & \\
\text{N} & \\
\text{H}_5\text{C}_2 & \\
\end{align*}
\]

The mixture is heated for 5 hours at 90°C, then precipitated in 1 liter of acetone. After drying, a soft resin is isolated, containing 23% by weight of condensed colored compound (λ = 555 nm and 425 nm).

Example 11

To 30.8 g (basic equivalent 0.167) of the resin described in Example 2, dissolved in 50 cc of MC, 150 cc of DMF
are added, containing 19.4 g (0.05 mole) of a colored compound of the formula:

\[
\text{ClH}_2\text{COCHNH}_2\text{CH}_2\text{C}
\]

The mixture is heated for 5 hours at 90°C, then poured into a large excess of acetone. After drying, a solid is obtained, containing 22% by weight of condensed colored compound.

**Example 12**

To 3.6 g of the cationic resin used in Example 2 (basic equivalent 0.0195), dissolved in 20 g of DMF, 7.6 g (0.0195 mole) of the following compound are added in solution in the DMF:

\[
\text{NH(CH}_2)_3\text{NHCOC}_2\text{Cl}
\]

The reaction medium is heated at 80-90°C for 8 hours and the appearing acidity is progressively neutralized with a
methanol solution of sodium methylate. The resin obtained is precipitated in 2 liters of acetone, then rinsed twice with 1 liter of solvent. There is thus obtained 8.3 g of blue resin soluble in water at a pH ≤ 6.5.

The quantity of fixed colored compound, determined by spectroscopy, is 37% by weight, with respect to the colored polymer of this invention.

Example 13

To 23 g (basic equivalent 0.29) of polyethylene-imine sold by the FLUKA Company under the name "Polymin P", dissolved in 40 g of dimethylformamide, 10 g of the colored compound of Example 1 are added, dissolved in the same solvent, then heated while agitating for 6 hours at 90°C. The colored resin is then isolated by precipitation in 2 liters of acetone.

After two washings with an excess of solvent, a dark red, water-soluble powder is obtained.

Example 14

In 65 cc of a 55:10 mixture of DMF/HCl, there are dissolved 9.65 g (basic nitrogen equivalent 0.052) of the resin described in Example 2, and 1.97 g (0.0052 mole), 1.65 g (0.0048 mole) and 2.13 g (0.0055 mole), respectively, of the following three colored compounds:

- (1) red colored compound (λ = 508 nm) of the formula:
(2) yellow colored compound ($\lambda_{\text{max}} = 468$ nm) of the formula:

(3) blue colored compound ($\lambda_{\text{max}} = 575$ and 619 nm) of the formula:

The solution is heated for 5 hours at $90^\circ$C. The resulting polymer is isolated by precipitation in 1 liter of acetone, giving a steel-gray solid. Thin layer chromatography is used to check that the colored polymer no longer contains
any detectable amount of the initial colored compound.

The proportion of condensed colored compound, measured by spectroscopy, is as follows:

<table>
<thead>
<tr>
<th>Condensed Colored Compound</th>
<th>Percent by Weight Relative to the Colored Resin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red</td>
<td>6.28</td>
</tr>
<tr>
<td>Yellow</td>
<td>5.76</td>
</tr>
<tr>
<td>Blue</td>
<td>6.89</td>
</tr>
</tbody>
</table>

**Example 15**

In 60 cc of a 45:15 DMF/Me mixture, there are dissolved 16.1 g (basic nitrogen equivalent 0.0869) of the resin described in Example 2 and 5 g (0.0174 mole) of a colored compound having the formula:

\[
\text{NH}(\text{CH}_2)_2\text{NICOCH}_2\text{Cl}
\]

\[
\begin{array}{c}
\text{NO}_2 \\
\text{OCH}_3
\end{array}
\]

The solution is heated for 5 hours at 90°C, then the resulting polymer is isolated by precipitation in 1 liter of acetone. It is a blue solid (\(\lambda = 478 \text{ nm}\)). Thin layer chromatography ensures that the colored polymer no longer contains any initial colored compound. The proportion of initial colored compound in the polymer, measured by spectroscopy, is 17.15% by weight.
Example 16

In 90 cc of a basic 80:10 mixture of DMF/HCl, there are dissolved 10 g (nitrogen equivalent 0.054) of the resin described in Example 2 and 4.8 g (0.016 mole) of a colored compound of the formula:

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{N} \\
& \quad \text{CH}_2\text{CH}_2\text{NHCOCH}_2\text{Cl} \\
& \quad \text{C}_6\text{H}_4\text{NO}_2 \\
& \quad \text{N}\text{HCH}_3
\end{align*}
\]

The mixture is heated for 5 hours at 90°C, then the polymer is isolated by precipitation in 1 liter of acetone. A purple powder is isolated (λ = 527 nm). Thin layer chromatography reveals the absence of free colored compound. The proportion of initial colored compound in the polymer, measured by spectroscopy, is 22.5% by weight.

Example 17

In 135 cc of a 120:15 DMF/HCl mixture, there are dissolved 10.5 g (basic nitrogen equivalent 0.0566) of the resin described in Example 2 and 1.8 g (0.045 mole), 3.3 g (0.011 mole) and 0.6 g (0.0016 mole), respectively, of the following three colored compounds:
(1) red colored compound \( \lambda = 505 \text{ nm} \) of the formula:

\[
\begin{align*}
\text{red compound:} & \quad \text{yellow colored compound:} \quad \text{blue colored compound:}
\end{align*}
\]

(2) yellow colored compound \( \lambda = 403 \text{ nm} \) of the formula:

(3) blue colored compound \( \lambda = 575 \text{ and } 619 \text{ nm} \) of the formula:

The solution is heated for 5 hours at 90°C, then the resulting colored polymer is precipitated in 500 cc of
acetone. After drying, a dark auburn solid is isolated.

Thin layer chromatography reveals no initial colored compounds.

The proportion of condensed colored compounds in the polymer, measured by spectroscopy, is as follows:

<table>
<thead>
<tr>
<th>Condensed Colored Compound</th>
<th>Percent by Weight Relative to the Colored Polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red</td>
<td>7.04</td>
</tr>
<tr>
<td>Yellow</td>
<td>14.2</td>
</tr>
<tr>
<td>Blue</td>
<td>2.1</td>
</tr>
</tbody>
</table>

Example 18

In 42 cc of a 35:7 DMF/HCl mixture, there are dissolved 7.15 g (basic nitrogen equivalent 0.0386) of the resin described in Example 2, and 2.5 g (0.0083 mole), and 1 g (0.0033 mole), respectively, of the following colored compounds:

1. purple colored compound ($\lambda_{\text{max}} = 527 \text{ nm}$) of the formula:

$$\text{H}_3\text{C-}\text{N-CH}_2\text{CH}_2\text{NHCOCH}_2\text{Cl}$$

2. yellow colored compound ($\lambda_{\text{max}} = 403 \text{ nm}$) of the formula:

$$\text{and}$$

-36-
The mixture is heated for 4 hours at 90°C. The resulting polymer is precipitated in 500 cc of acetone. A brown solid, free from initial colored compounds, is obtained as verified by thin layer chromatography. The polymer has the following proportion of condensed colored compounds, measured by spectroscopy:

<table>
<thead>
<tr>
<th>Condensed Colored Compound</th>
<th>Percent by Weight Relative to the Colored Polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purple</td>
<td>14.32</td>
</tr>
<tr>
<td>Yellow</td>
<td>6.36</td>
</tr>
</tbody>
</table>

Example 19

To 576 g of an ethanol solution containing 76.5 g (0.5 mole) of 2-nitroparaphenylenediamine, there are rapidly added 99.9 g (1.08 mole) of epichlorohydrin. The resulting mixture is then heated for 10 hours at solvent reflux. The solvent as well as free epichlorohydrin are removed by evaporation under reduced pressure.

To 30 g of the above synthesized compound, dissolved
in 500 cc of methyl cellosolve, 56.8 g (0.66 mole) of piperazine in a 50% solution in the same solvent are added. The resulting reaction medium is heated for 3 hours at 90°C. The hydrochloric acid formed is then neutralized with 16.7 g of 40% NaOH. There are then added 46.5 g (0.5 mole) of epichlorohydrin, drop by drop, over a 20 minute period. The reaction medium is then heated for 1-1/2 hours at 90°C.

The resulting polymer is precipitated by the addition of 3 liters of acetone. After drying, a powdery solid, soluble in water at a pH lower than 7.5 is obtained. Thin layer chromatography reveals no free initial colored compound.

The proportion of initial colored compound in the polymer, measured by spectroscopy, is 8.79 % weight.

The polymer can be represented by the following formula:

\[
\begin{align*}
\text{CH}_2\text{CHOHCH}_2\text{-N-CH}_2\text{CHOHCH}_2\text{-N} & \quad \text{N} \\
\text{CH}_2\text{CHOHCH}_2\text{-N} & \quad \text{N}
\end{align*}
\]

with \( n/n' \) = 0.17.

Example 20

To 2,643 g of an aqueous solution containing 185.2 g (basic equivalent 1) of the polyaminoamide described in Example 2, there are added with stirring, over a 1 hour period at 20°C,
87.9 g (0.95 mole) of epichlorohydrin. The solution is
maintained with stirring for 1 hour at that temperature, and
then for 1 hour at 90°C.

To 250 g of the above solution, reduced to 125 g
by evaporation of the water, there are added 71 g of an
acetonitrile solution containing 7.1 g (0.043 mole) of a
colored compound having the formula:

\[
\text{NH}_2
\]
\[
\text{NHCH}_3
\]
\[
\text{NO}_2
\]

The resulting reaction medium is heated for 3 hours at 80°C.
The free colored compound is removed from the aqueous solution
by extraction, initially with chloroform and then with ether.
After evaporation of the remaining organic solvent, the 5%
solution of active material is added to water. Thin layer
chromatography reveals no free colored compound. The proportion
of fixed colored compound on the polymer, measured by spectroscopy,
is 15% by weight.

**Example 21**

In 14 cc of methyl"Cellosolve," 3.6 g (basic equivalent
0.019) of the resin described in Example 2 and 1 g (0.0039 mole)
of a colored compound of the following formula are dissolved:
The resulting reaction medium is heated for 5 hours at 90°C. The polymer is isolated by precipitation in acetone. It is a light brown solid (λ = 396 nm). It is free of initial colored compound as verified by thin layer chromatography. The amount of colored compound in the polymer, measured by spectroscopy, is 18% by weight.

Example 22

To 10.2 g of a solution of methyl "Cellosolve" containing 3.06 g (basic equivalent 0.0165) of the resin used in Example 14, there are added 1.225 g (0.05 mole) of N-bromoethyl paranitraniline, dissolved in 20 cc of dimethylformamide. The resulting mixture is heated for 5 hours at 90°C. The resulting polymer is precipitated in 500 cc of acetone, yielding a yellow polymer (λ = 394 nm), free of initial colored compound as verified by thin layer chromatography. The polymer contains 15.5% by weight of the initial colored compound, measured by spectroscopy.
Example 23

A hair dye composition is prepared by admixing the following components:

Polymer of Example 6 ........................ 0.07 g
Polymer of Example 12 ........................ 0.055 g
Vinyl acetate crotonic acid copolymer (90:10)
M.W. 45,000 - 50,000 ..................... 1.5 g
Vinylpyrrolidone-vinyl acetate copolymer (60:40)
viscosity 3.3-4 cps, M. W.
45,000 - 60,000 ........................ 0.25 g
Ethyl alcohol, sufficient for ...... 50°
Triethanolamine, sufficient for .... pH 7
Water, sufficient for ............... 100 cc

This hair setting lotion, when applied to deep blond hair, imparts thereto an especially pleasing pretty dark blond shade.

Example 24

A hair dye composition is prepared by admixing the following components:

Polymer of Example 12 ........................ 0.0325 g
Vinyl acetate crotonic acid copolymer (90:10)
M.W. 45,000 - 50,000 ..................... 1.5 g
Vinylpyrrolidone-vinyl acetate copolymer (60:40)
viscosity 3.3-4 cps,
M.W. 45,000 - 60,000 ..................... 0.25 g
Ethyl alcohol, sufficient for ...... 50°
Triethanolamine, sufficient for .... pH 7
Water, sufficient for ............... 100 cc

This hair setting lotion, when applied to chestnut colored hair, imparts thereto a very pretty ash-chestnut shade.

Example 25

A hair dye composition is prepared by admixing the following components:

<table>
<thead>
<tr>
<th>Component</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer of Example 5</td>
<td>0.18 g</td>
</tr>
<tr>
<td>Vinyl acetate crotonic acid copolymer (90:10)</td>
<td>1.5 g</td>
</tr>
<tr>
<td>M. W. 45,000 - 50,000</td>
<td></td>
</tr>
<tr>
<td>Vinylpyrrolidone-vinyl acetate copolymer (60:40)</td>
<td>0.25 g</td>
</tr>
<tr>
<td>viscosity 3.3-4 cps, M.W. 45,000 - 60,000</td>
<td></td>
</tr>
<tr>
<td>Ethyl alcohol, sufficient for ...... 50°</td>
<td></td>
</tr>
<tr>
<td>Triethanolamine, sufficient for...... pH 7</td>
<td></td>
</tr>
<tr>
<td>Water, sufficient for ............... 100 cc</td>
<td></td>
</tr>
</tbody>
</table>

When applied to light chestnut colored hair, this hair-setting lotion imparts to the hair especially attractive iridescent ashen glints.

Example 26

A hair dye composition is prepared by admixing the following components:

<table>
<thead>
<tr>
<th>Component</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer of Example 1</td>
<td>0.04 g</td>
</tr>
<tr>
<td>Polymer of Example 5</td>
<td>0.05 g</td>
</tr>
</tbody>
</table>
Polyvinylpyrrolidone,  
M.W. = 40,000 .................. 0.05 g
Trimethylcetylammonium bromide ..... 0.2 g
Quaternized polyvinylpyrrolidone,  
sold under the tradename  
"GAFQUAT 734" (active matter) ... 0.4 g
Ethyl alcohol, sufficient for ...... 120 g
Triethanolamine, sufficient for .... pH 7
Water, sufficient for ............. 100 cc
This rinse is applied to hair colored very light blond. After drying, the hair untangles easily and has a particularly shiny and esthetic silvery blond shade.

Example 27

A hair dye composition is prepared by admixing the following components:

Polymer of Example 2 ................. 0.35 g
Polymer of Example 4 ................. 0.1 g
Vinylpyrrolidone-vinyl acetate copolymer (60:40)  
viscosity 3.3-4 cps,  
M.W. 45,000 - 60,000 ............... 0.5 g
Trimethylcetylammonium bromide ..... 0.1 g
H₂O₂ (20 vol), sufficient for ...... 10 vol.
Orthophosphoric acid, sufficient for pH 3
Water, sufficient for ................. 100 cc
When applied to natural deep blond hair, this lotion, after drying, imparts thereto a light sheen with pretty auburn glints.

**Example 28**

A hair dye composition is prepared by admixing the following components:

- Polymer of Example 6 ................. 0.5 g
- Sodium laurylsulphate with 30% active ingredients sold under the name "DELP 8533" ...................... 25 g
- Butyl "Cellosolve" ...................... 10 g
- Copra diethanolamide ................... 5 g
- Citric acid, sufficient for ....... pH 6
- Water, sufficient for .............. 100 cc

Natural light chestnut colored hair, when shampooed with this composition, after rinsing and drying, has very lustrous mahogany glints.

**Example 29**

A hair dye composition is prepared by admixing the following components:

- Polymer of Example 12 ................. 0.325 g
- Polymer of Example 2 ................. 0.775 g
- Trimethylcetylammonium bromide ...... 5 g
Lauryl alcohol oxyethylenated with 12.5 moles of ethylene oxide, sold under the name "FREPAL 12" 4 g

Citric acid, sufficient for pH 4

Water, sufficient for 100 cc

Bleached hair, when shampooed for 15 minutes with this composition, after rinsing and drying, has a particularly esthetic looking pearly shade.

Example 30

A hair dye composition is prepared by admixing the following components:

Polymer of Example 3 0.85 g

Hydroxyethylcellulose sold under the name "CELLOSIZE 3" 3.52 g

Citric acid, sufficient for pH 6

Water, sufficient for 100 cc

When applied for 20 minutes to blond hair, this composition, after rinsing and drying, imparts thereto a very lovely ash-blond shade.

Example 31

A hair dye composition is prepared by admixing the following components:

Polymer of Example 2 7.75 g
Hydroxyethylcellulose sold under the name "CELLOSIZE WP 3" 3.52 g
Citric acid, sufficient for pH 6
Water, sufficient for 100 cc

When applied for 15 minutes to chestnut colored hair, this composition, after rinsing and drying, imparts thereto very original, pretty rose glints.

**Example 32**

A hair dye composition is prepared by admixing the following components:

- Polymer of Example 4 1 g
- Butyl "Cellosolve" 8 g
- Propylene glycol 8 g
- Alkylphenol polyethoxyether, sold under the name "REMCOPAL 334" 22 g
- Alkylphenol polyethoxyether, sold under the name "REMCOPAL 349" 22 g
- Ammonia - 22° Bé 10 cc
- Water, sufficient for 100 g

Twenty grams of water are added to 20 g of the above solution, giving a gel which is applied to light blond colored hair. The gel is permitted to remain in contact with the hair for 20 minutes. Thereafter the hair is washed. After drying, the hair has very pretty ash-blond glints.
Example 33

A hair dye composition is prepared by admixing the following components:

- Polymer of Example 1 ................. 2.4 g
- Polymer of Example 2 ................. 3.1 g
- Polymer of Example 4 ................. 0.25 g
- Butyl "Cellosolve" ..................... 8 g
- Propylene glycol ...................... 8 g
- Alkylphenol polyethoxyether, sold under the name "REMCOPAL 334" .......... 22 g
- Alkylphenol polyethoxyether, sold under the name "REMCOPAL 349" .......... 22 g
- Ammonia - 22° Be' .................... 10 cc
- Water, sufficient for ............... 100 g

Twenty grams of water are added to 20 g of the above solution. A gel is obtained that is applied for 30 minutes to deep chestnut colored hair. After rinsing and drying, the hair exhibits particularly esthetic lilac glints.

Example 34

A hair dye composition is prepared by admixing the following components:

- Polymer of Example 2 ................. 3 g
- Polymer of Example 3 ................. 0.3 g
- Butyl "Cellosolve" ..................... 8 g
Propylene glycol ....................... 8 g
Alkylphenol polyethoxyether,
sold under the name
"REMCOPAL 334" ........................ 22 g
Alkylphenol polyethoxyether,
sold under the name
"REMCOPAL 349" ........................ 22 g
Ammonia - 22° Bé ....................... 10 cc
Water, sufficient for .................. 100 g

Twenty grams of H₂O₂ (20 volumes) are added to 20 g
of the above prepared solution. This gives a gel which is
applied to blond hair. After 30 minutes contact time, the
hair is washed and becomes lighter in color with a slightly
iridescent, lovely pearly luster.

Example 35

A hair dye composition is prepared by admixing the
following components:

Polymer of Example 16 .................... 0.4 g
Vinyl acetate crotonic acid copolymer (90:10)
M.W. 45,000 - 50,000 ................... 1.5 g
Vinylpyrrolidone-vinyl acetate
copolymer (60:40)
viscosity 3.3 - 4 cps,
M.W. 45,000 - 60,000 .................. 0.25 g
Ethyl alcohol, sufficient for ...... 50°
Tartaric acid, sufficient for ...... pH 6
Water, sufficient for ................. 100 cc
When applied to partially white blond hair, this hair setting lotion imparts thereto very pleasing lilac glints and a partially de-yellowing effect.

**Example 36**

A hair dye composition is prepared by admixing the following components:

- Polymer of Example 17 ................. 0.375 g
- Vinyl acetate crotonic acid copolymer (90:10) M.W. 45,000 - 50,000 ............ 1.5 g
- Vinylpyrrolidone-vinyl acetate copolymer (60:40) viscosity 3.3-4 cps, M.W. 45,000 - 60,000 ............ 0.25 g
- Ethyl alcohol, sufficient for ...... 50°
- Tartaric acid, sufficient for ...... pH 6
- Water, sufficient for .............. 100 cc

When applied to naturally deep chestnut colored hair, this hair setting lotion imparts to the hair very beautiful mahogany glints.

**Example 37**

A hair dye composition is prepared by admixing the following components:

- 4-N-γ-amino-propyl-amino-
  1-N'-methylamino
  anthraquinone ................. 0.145 g
- Polymer of Example 16 ............. 1.14 g
Polymer of Example 21 ................ 1.464 g
Vinyl acetate crotonic acid
copolymer (90:10)
M.W. 45,000 - 50,000 ............. 1.5 g

Vinylpyrrolidone-vinyl acetate
copolymer (60:40)
Viscosity 3.3-4 cps,
M.W. 45,000 - 60,000 ............. 0.25 g

Ethyl alcohol, sufficient for ...... 50°

Tartaric acid, sufficient for ...... pH 6

Water, sufficient for.............. 100 cc

When applied to light chestnut colored hair, this solution gives the hair an extremely natural light chestnut shade.

Example 38

A hair dye composition is prepared by admixing the following components:

Polymer of Example 14 ............. 0.366 g

Vinyl acetate crotonic acid
copolymer (90:10)
M.W. 45,000 - 50,000 ............. 1.5 g

Vinylpyrrolidone-vinyl acetate
copolymer (60:40)
Viscosity 3.3-4 cps,
M.W. 45,000 - 60,000 ............. 0.25 g

Penzylidene camphor ............. 0.3 g

Ethyl alcohol, sufficient for ...... 50°

Tartaric acid, sufficient for ...... pH 6

-50-
Water, sufficient for ............... 100 cc

When applied to grey hair which is 90% white, this hair setting lotion restores the proper sheen, with an especially luminous and esthetic looking iridescent color.

Example 39

A hair dye composition is prepared by admixing the following components:

Aqueous solution (5%, pH 4.5) of the hydrochloride of the polymer of Example 20 ........ 2.22 g

Polyvinylpyrrolidone, M.W. = 40,000 ....................... 0.5 g

Trimethylcetylammonium bromide ...... 0.2 g

Quaternized polyvinylpyrrolidone, sold under the name "GAFQUAT 734" (active ingredients) ......................... 0.4 g

Ethyl alcohol, sufficient for ........ 12°

Tartaric acid, sufficient for ........ pH 5.5

Water, sufficient for ............... 100 cc

This rinse is applied to light blond hair. After drying, the hair easily untangles and has a lovely light blond shade with a slightly pearly sheen.

Example 40

A hair dye composition is prepared by admixing the following components:
Polymer of Example 15 ............... 1.5 g

Vinylpyrrolidone-vinyl acetate
copolymer (60:40)
viscosity 3.3-4 cps,
M.W. 45,000 - 60,000 ............... 0.5 g

Trimethylcetylammonium bromide .... 0.1 g

H₂O₂ (200 volumes), sufficient for . 10 vol.
Ethyl alcohol, sufficient for ........ 55°
Orthophosphoric acid, sufficient for pH 3
Water, sufficient for ............... 100 cc

When applied to natural light chestnut colored hair, this lotion, after drying, brightens the hair and gives it particularly warm and luminous copper glints.

Example 41

A hair dye composition is prepared by admixing the following components:

Polymer of Example 14 ............... 0.736 g

Hydroxyethylcellulose, sold
under the name of
"CELLOSIZE WP 3" ............... 3.3 g

Citric acid, sufficient for ........... pH 6
Water, sufficient for ............... 100 g

When applied for 20 minutes to hair which has previously been bleached light blond, this composition, after rinsing with water, shampooing and drying, gives the hair a beautiful ash-blond shade.
A hair dye composition is prepared by admixing the following components:

**Polymer of Example 17** ............... 2 g

"SIPOL SX" wax (mixture of fatty alcohols C_{16}-C_{18} (90\% by wt.) and sodium lauryl sulphate (10\% by wt.)) ........................................... 2 g

"UKANIL 25" [fatty alcohol \((C_{13}-C_{15})\) oxyethylenated with 2.8 moles of ethylene oxide] ........................................... 3 g

"UKANIL 43" [fatty alcohol \((C_{13}-C_{15})\) oxyethylenated with 7 moles of ethylene oxide] ........................................... 2 g

Trimethylcetyl ammonium bromide .... 1.5 g

Ethyl "Collosolve" ..................... 10 cc

Citric acid, sufficient for .......... pH 8

Water, sufficient for ............... 100 g

90 grams of this mixture are incorporated into an aerosol container together with 10 g of a propellant mixture comprising 43 parts of 1,2-dichloro-1,1,2,2-tetrafluoro ethane and 57 parts of dichlorodifluoromethane. About 25 g of this foam are applied to blond hair and 10 minutes later, after rinsing in warm water and drying, the hair becomes consistently and discreetly colored mahogany blond.
A hair dye composition is prepared by admixing the following components:

Polymer of Example 7 .......................... 1.7 g
Polymer of Example 16 ......................... 0.26 g
Polymer of Example 17 ......................... 13.6 g
Alkylphenol polyethoxyether sold under the name "REMCOPAL 334" ....................... 22 g
Alkylphenol polyethoxyether sold under the name "REMCOPAL 349" ....................... 22 g
Propylene glycol .................. ............. 14 g
Pentasodium salt of diethylene-triaminepentacetic acid sold under the name "NASQUOL DTPA" ... 2.5 g
Ammonia 22° Bé ................................. 7 cc
Water, sufficient for ......................... 100 g

Just before use, 20 g of a H₂O₂ solution (6% by weight) are incorporated into 20 g of this gel. A jellified liquid is then obtained which is applied for 30 minutes to blond hair that has been somewhat sensitized by prior treatments. After rinsing in warm water and drying, the hair has a very luminous light mahogany coppery blond color.

A hair dye composition is prepared by admixing the following components:
Paratoluylene diamine .................. 0.15 g
Paraaminophenol ......................... 0.35 g
2-methyl-5-N-β-hydroxyethyl-
aminophenol .............................. 0.45 g
Polymer of Example 15 .................. 12 g
Alkylphenol polyethoxyether
sold under the name
"REMCPAL 334" ........................... 22 g
Alkylphenol polyethoxyether
sold under the name
"REMCPAL 349" ........................... 22 g
Butyl "Cellosolve" .......................... 8 g
Propylene glycol ........................... 8 g
Ethylene-diamine-tetraacetic acid .. 0.2 g
Hydroquinone .............................. 0.2 g
Sodium acid sulphite, 36° Bé .......... 1 cc
Ammonia 22° Bé ............................ 10 cc
Water, sufficient for .................... 100 cc

Just before use, 20 g of this semi-transparent liquid
are mixed with 20 g of a H₂O₂ solution (6% by weight) and the
resulting gel is applied to very light blond hair which is
90% white. After rinsing with water, shampoo and drying,
the hair is dyed a slightly iridescent coppery golden blond
color.
THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A dye comprising a water-soluble cationic polymer, having a molecular weight ranging between approximately 800 and 100,000 and having secondary, tertiary or quaternary ammonium amine groups, wherein said amine groups are either part of, or aid in the direct or indirect linking to the polymer chain, an aryl or arylaliphatic chromophore or chromogen group carrying compound, with the proviso that when the main chain of the polymer has amine groups derived from said chromophore or chromogen group carrying compound, the said main chain must also have at least 10% aliphatic amine groups relative to the total number of amine groups of the said chain.

2. The dye of claim 1 wherein the polymer skeleton, apart from the said chromophore or chromogen group carrying compound residue is derived from a cationic polycondensate which is a keratinic fiber conditioner.

3. The dye of claim 1 wherein amine groups which are derived from chromophore or chromogen group carrying compounds represent from 5 to 100% of the total number of amine groups of the polymer chain.
4. The dye of claim 1 wherein the cationic polymer is a non-reticulated linear or branched polymer.

5. The dye of claim 1 wherein the cationic polymer is a slightly reticulated polymer.

6. A process for producing the dye of claim 1 comprising reacting at least one reactive colored compound with at least one cationic resin having primary, secondary or tertiary alkylatable amine groups.

7. The process of claim 6 wherein the cationic resin is a polyamine or a polyaminoamide.

8. The process of claim 7 wherein the reactive colored compound is a chromophore or chromogen group carrying compound having mobile chlorine or bromine atoms or having epoxide groups or having double activated bonds.

9. The process of claim 6 wherein the said reactive colored compound includes one or more -NHCOCH₂Cl radicals.

10. The process of claim 9 wherein said reactive compound results from the chloraceteylation of a dye having one or more aromatic amine functions replaced by an aminoalkyl
radical or having one or more aminoalkoxy substitutions, with the proviso that only the extranuclear amine functions are chloroacetylated.

11. The process of claim 10 wherein the chloroacetylated reactive compound is derived from a nitro benzene dye, an anthraquinone dye, an azo dye, an indamine, an indoaniline, an indophenol, or a 1,4-benzoquinone dye.

12. The process of claim 6 wherein the reactive colored compound is derived from a nitro benzene dye, an anthraquinone dye, an azo dye, an indamine, an indoaniline, an indophenol, or a 1,4-benzoquinone dye.

13. The process of claim 6 wherein the reactive colored compound has one or more aromatic amine groups replaced by ω-halogenoalkyl, 3-chloro-2-hydroxy propyl or 2,3-epoxy propyl radicals.

14. The process of claim 6 wherein the reactive colored compound has at least one halogenoalkoxy group on an aromatic nucleus.

15. The process of claim 6 wherein the reactive colored compound has a chloro-triacylvinyl group.

16. The process of claim 6 wherein the reactive colored compound has a vinyl-sulphone group.

17. A process for producing the dye of claim 1 comprising reacting a colored compound having alkylatable phenol or amine groups with a cationic polymer having reactive groups.
17. The process of claim 16 wherein the cationic polymer having reactive groups is the reaction product of an epihalohydrin with a polyamino amide resulting from the polycondensation of a diacid and a polyamine of the formula \[ \text{H}_2\text{N} \left(\text{CH}_2\text{CH}_2\text{NH}\right)_{\text{n}} \text{H}, \] wherein the value of \( n \) is 2 or 3.

18. The process of claim 17 wherein the epihalohydrin is present in an amount ranging from about 0.8-1.3:1 relative to the basic groups, the resin obtained having azetidinium, halohydrin or epoxide groups.

19. The process of claim 6 wherein the reaction of the reactive colored compound with the cationic resin is carried out in the presence of a solvent selected from an alcohol solvent, an aromatic solvent, dimethylformamide or acetonitrile, at temperatures ranging between 30 and 130°C for a period of time ranging between approximately 1 and 10 hours.

20. A process for producing the dye of claim 1 comprising reacting at least one dialkylatable aminated compound with at least one other bifunctional compound having functions reactable with an amine, one of the two said reacting compounds being a chromophore or chromogen group carrying compound.
21. The process of claim 20 wherein the functions of the bifunctional compound reactable with an amine are selected from epoxide functions, halide functions or double activated bonds.

22. The process of claim 20 wherein the bifunctional compound is employed in the presence of piperazine.

23. The process of claim 20 wherein the bifunctional compound is a di-halogeo-alkane or di-halohydrin derivative and the dialkylatable aminated compound is a secondary or tertiary diamine.

24. The process of claim 20 wherein the bifunctional compound is selected from 3-chloro-2-hydroxy piperazine, 2,3-epoxy piperazine, di-acryloyl-piperazine, ethylene diamine diglycidyl ether or ethylenediamine diacrylamide.

25. The process of claim 20 wherein the reaction is effected in water, in a solvent or in a water-solvent mixture at a temperature ranging between 50 and 150°C for a period of time ranging between about 1 and 10 hours.

26. A compound obtained in accordance with the process of claim 6.

27. A compound obtained in accordance with the process of claim 16.
28. A compound obtained in accordance with the process of claim 20.

29. A dye composition for dyeing keratinic material comprising in solution at least one dye of claim 1.

30. The composition of claim 29 wherein said dye is present in an amount ranging from 0.01 to 10 percent by weight based on the total weight of the composition.

31. The composition of claim 29 having a pH between 1 and 11.

32. The composition of claim 29, which also includes an azo dye, an anthraquinone dye, a nitrobenzene dye, a 2,5-diaminoquinone, an indophenol, an indoaniline, an indamine, a phenylamine, or an oxidation base and a coupler.

33. The composition of claim 29 which also includes an alkalizing or acidifying agent and one or more of an oxidation agent, a solvent, a polymer, a cationic-type agent, an anide, a thickener, a surfactant, a sun filter, an optical bluing agent, an antioxidizing agent, a sequesterant or a perfume.
34. A compound of the formula

$$A-[\text{NR}-(\text{CH}_2)_n-\text{NHCOCH}_2\text{Cl}]_p$$

wherein \(R\) is alkyl containing from 1 to 3 carbon atoms; 
\(p\) is a whole number between 1 and 3, inclusive; \(n\) is a 
whole number between 1 and 4, inclusive, with the proviso 
that the values of \(n\) for each of the \(p\) groups attached to 
nucleus \(A\) can be equal or different; and \(A\) represents a 
substituted or unsubstituted residue of a nitrobenzene dye, 
an anthraquinone dye, an azo dye, an indamine, an indocate, 
an indophenol, a 1,4-benzoquinone dye or an \(A-B\) dye derived 
from the covalent bonding of compounds \(A\) and \(B\) which are dyes 
per se or dye generators of the benzene, anthraquinone or 
azo series.

35. The compound of claim 35 selected from 
3-nitro-4-\(N\)-\(\beta\)-chloroacetaminoethylamino anisole, 
4-nitro-\(N\)-\(\beta\)-chloroacetaminoethylamine, 
1-methylamino-2-nitro-4-(\(N'\)-methyl, \(N'\)-\(\beta\)-chloroacetamino- 
ethyl) amino benzene, 
1-dimethylamino-3-\(N\)-\(\beta\)-chloroacetaminoethylamino-4-nitro 
benzene 
1-\(\gamma\)-chloroacetaminoethylamino-4-\(N\)-methylamine anthraquinone, 
1-hydroxy-4-\(\gamma\)-chloroacetaminoethylamino anthraquinone,
2-β-chloroacetylaminooethylamino anthraquinone,
1-γ-chloroacetylaminopropylamino anthraquinone,
the azo compound of 2-amino benzothiazole and N-ethyl,
N-β-chloroacetylaminooethylaniline,
N[[4-(ethyl-β-chloroacetylaminooethyl)amino]phenyl] 2,6-
dimethyl-3-amino benzoquinone imine, and
2-N-β-hydroxyethylamino-5 (4-N-ethyl, N-β-chloroacetylaminoo-
ethylamino anilino)-1,4-benzoquinone.

Dated this 8th day of August 77

LOREAL

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