United States Patent Office

3,100,704

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3,100,704
PHOTOGRAPHIC MATERIALS CONTAINING CARBODIIMIDES

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17 Claims. (Cl. 96—111)

This invention relates to photography, and particularly, to photographic gelatin layers and light-sensitive photographic gelatin emulsion layers containing the quaternary ammonium salts of an N,N'-disubstituted carbodiimide as a hardening agent.

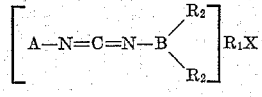
Gelatins used in the production of photographic materials have been reacted with a variety of hardening and modifying agents such as alum, chrome alum; formaldehyde, glyoxal or other aldehydes; keto-alcohols, nitroaldehydes, nitroureas, and the like to improve the physical characteristics of the gelatins. In all cases, however, the reagents react with the gelatin to yield a derivatized gelatin containing the reagent or a part thereof as an integral part of the gelatin structure with the result that some questionable improvement in physical properties is accompanied by an impairment of photographic properties.

It is an object of our invention to prepare hardened photographic gelatin layers, having improved physical and photographic characteristics.

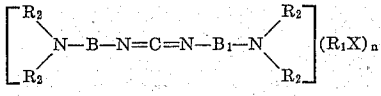
Other objects will be apparent from the following description.

We have found that compositions of matter adapted to form hardened gelatin layers including gelatin silver halide emulsion layers can be prepared by using the products resulting from the addition to an aqueous gelatin solution of a small portion of a quaternary ammonium salt of an N,N'-disubstituted carbodiimide. These layers have new and improved properties, display unique characteristics and differ from unreacted gelatin and silver halide emulsion layers by their melting points and photographic characteristics.

The water or alcohol soluble quaternary ammonium salts of the N,N'-disubstituted carbodiimdes used in accordance with this invention are characterized by the following general formulae:



and



wherein A represents an organic radical such as an aliphatic radical, e.g., methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, tert.-butyl, allyl, crotyl, β-hydroxyethyl, methoxy-methyl-β-bromoallyl, and the like; an aromatic radical, e.g., phenyl, tolyl, xylyl, naphthyl, chlorophenyl, bromophenyl, iodophenyl and the like; and alicyclic radical, e.g., cyclohexyl, bornyl, menthyl and the like; and a heterocyclic radical, e.g., pyridyl, quinolyl and the

like; R_1 and R_2 are lower alkyl radicals, e.g., methyl, ethyl, propyl, isopropyl, butyl and the like; B and B_1 which may be alike or different represent alkylene, arylene or aralkylene radicals, e.g., propylene, phenylene, tolylene, propylphenylene and the like; X is an anion, e.g., chloride, bromide, iodide, methosulfate, ethosulfate, p-toluenesulfonate; and *n* is a positive integer not greater than 2.

The disubstituted carbodiimides are prepared by treating an N,N'-disubstituted symmetrical or unsymmetrical thiourea, having at least one tertiary amino group, with a desulfurizing agent, particularly the oxide of a heavy metal such as lead or mercury, as described in Berichte, vol. 71, pages 1512–21; vol. 73, pages 467–477, 1114–1123; vol. 74, pages 1285–1296 and vol. 75, pages 100–5; Annalen, vol. 560, pages 222–231; also Journal of Organic Chemistry, vol. 21, pages 1024–6.

The N,N'-disubstituted carbodiimides with the tertiary amino group are converted into the quaternary ammonium salt by reacting them directly, or in the presence of a solvent-diluent such as ethyl acetate, chloroform, benzene, or toluene, or mixtures thereof, with a suitable quaternizing agent such as methyl bromide, ethyl bromide, methyl iodide, ethyl iodide, dimethyl sulfate, diethyl sulfate, methyl p-toluene sulfonate, ethyl p-toluene sulfonate and the like. Molar equivalents of the quaternizing agent or a slight excess thereof are employed if only one of the tertiary nitrogen atoms is to be quaternized while di-molar equivalents are used when two tertiary amino groups are to be converted into the quaternary forms.

The following is a suggestive listing of N,N'-disubstituted carbodiimides which may be employed for the purpose herein set forth:

N-isopropyl-N'-(4-dimethylaminophenyl)carbodiimide ethyl p-toluenesulfonate

N-phenyl-N'-(4-dimethylaminophenyl)carbodiimide ethyl p-toluenesulfonate

N,N'-di(4-dimethylaminophenyl)carbodiimide monoethobromide

N,N'-di(4-dimethylaminophenyl)carbodiimide monoethiodide

N,N'-di(4-dimethylaminophenyl)carbodiimide dimethiodide

N,N'-di(4-diethylaminophenyl)carbodiimide methyl p-toluenesulfonate

N,N'-di(4-dipropylaminotolyl)carbodiimide ethyl p-toluenesulfonate

N,N'-di(4-dimethylaminophenyl)carbodiimide monomethosulfate

N,N'-di(4-dimethylaminophenyl)carbodiimide dimethosulfate

N,N'-di(4-dimethylaminophenyl)carbodiimide ethyl p-toluenesulfonate

N-bornyl-N'-(4-dimethylaminophenyl)carbodiimide methosulfate

N-menthyl-N'-(4-dimethylaminophenyl)carbodiimide ethosulfate

N-(β-bromoallyl)-N'-(γ-dimethylaminopropyl)carbodiimide ethosulfate

N-(tert.-butyl)-N'-(γ-dimethylaminopropyl)carbodiimide ethyl p-toluenesulfonate

N-cyclohexyl-N'-(4-dimethylaminophenyl)carbodiimide ethyl p-toluenesulfonate

N-isopropyl-N'-(γ-dimethylaminopropyl)carbodiimide ethobromide

N-methoxymethyl-N-(γ-dimethylaminopropyl)carbodiimide ethyl p-toluenesulfonate

N,N'-di-(γ-pyridyl)carbodiimide monomethosulfate

N,N'-di-(γ-pyridyl)carbodiimide diethosulfate

The reaction between the gelatin (bone, hide, pigskin or degraded, etc.) and the carbodiimide can be carried out by dissolving or swelling the gelatin in water and then adding the quaternary ammonium salt of the carbodiimide in any convenient inert solvent media, preferably water, alcohol, or mixtures thereof.

The gelatin concentration may vary over a wide range, e.g., from 0.5 to 20 percent by weight. The amount of carbodiimide quaternary ammonium salt employed in the reaction may range from 5 gms. to 50 gms. per kg. of dry gelatin although amounts ranging from 10 to 25 gms. of carbodiimide per kg. of dry gelatin are preferred. The reaction temperature may be varied from 5° C. to 75° C., preferably from 15 to 50° C., but care must be taken to avoid prolonged heating at such higher temperatures at which the gelatin becomes unstable. The pH may be varied through the mildly acid or mildly alkaline range although a pH between 5 and 8 has been found most suitable in aqueous systems.

The gelatin solutions and photographic emulsions which have been hardened with the carbodiimide quaternary salts yield products which have valuable properties. They yield photographic films which have higher melting points and which are less affected by storage and processing at elevated temperatures. The viscosity of the gelatin solution containing the carbodiimide is not increased on holding prior to coating, so that no compensation must be made to correct for constantly increasing viscosities prior to and during the coating operation. Most important is the feature that emulsions hardened with our quaternary ammonium salts are free from fog and do not suffer from loss of speed and contrast, but actually show a mild speed increase during storage. Furthermore, the quaternary salts do not cause the undesirable effects known as "after hardening" but reach a stabilized melting point within a few days of storage at room temperature.

Our procedure offers special advantages when applied to gelatins which contain substantial amounts of degradation products. Such materials frequently have desirable photographic properties, but cannot be used commercially in view of their poor physical properties. Such gelatins can be substantially improved with our process through relinking of the degradation products to the parent gelatin molecules. More particularly, gelatin samples which contain substantial amounts of degradation products are characterized by depreciated properties, such as lowered melting points and setting points, decreased rigidity moduli (meaning the resistance of gelatin gels to deformation) increased Bloom value (measuring the resistance of the surface to penetration) as described in the "Encyclopedia of Chemical Technology," vol. VII, page 151 (1951) increased brittleness and increased water solubility. These deficiencies are ameliorated by the treatment with carbodiimides.

The reaction between the gelatin and the carbodiimide is believed to be attained in such a way that the carbodiimide may serve solely as a condensing or cross-linking agent as illustrated by the following hypothetical general equation in which the symbol "gel" represents the residue of a gelatin molecule for reasons of simplicity:

$$H_2N\text{-Gel-}CO_2H + H_2N\text{-Gel-}COOH \xrightarrow[\text{ammonium salt}]{\text{carbodiimide quaternay}} H_2N\text{-Gel-}CONH\text{-Gel-}COOH$$

Since gelatin contains both free amine and free carboxyl groups, this type of reaction may be either an intra- or intermolecular condensation. Only gelatin molecules are involved in cross-linking. Obviously, this reaction need not stop with two gelatin molecules but can involve

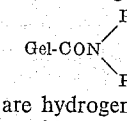
several. It will be observed that this reaction differs entirely from the type of modification of gelatin obtained by the use of conventional hardeners such as formaldehyde, keto-alcohols, etc., because the latter enter the gelatin molecule or form the cross-links which bind the gelatin molecules.

The materials obtained by our procedure can be further modified by the use of external acids such as acetic, butyric, stearic, or other aliphatic acids; by benzoic, toluic, or other variously substituted aromatic acids; or by alicyclic or heterocyclic carboxylic acids. These acids are caused to react with the amino groups of gelatin by the use of carbodiimides as condensing agents. The reaction is analogous to those which occur when carbodiimides are mixed with gelatin alone, and the reaction products are assumed to have the following general formula:

$$Gel\text{—}NH\text{—}COR$$

wherein R is the residue of the carboxylic acid used in the reaction.

The same reasoning applies to the case of reacting gelatins with amines such as ammonia, methylamine, diethylamine, aniline or other primary or secondary amines while using a carbodiimide as the condensing agent. In this case, the amines react with the carboxyl groups of gelatin to yield the following type of compound:



wherein R_1 and R_2 are hydrogen or hydrocarbon radical and constitutes the residue of the amine used in the reaction.

Our invention includes in one of its preferred forms the use of carbodiimide quaternary ammonium salts in conjunction with conventional gelatin hardeners such as formaldehyde, glyoxal, glycol aldehydes, diketones, halogen-substituted aldehyde acids such as mucochloric acid and mucobromic acid, formylacrylic acid, glyoxylic acid, halogen-substituted ketones such as chloroacetone, dichloroacetone or dibromoacetone, hydroxy-substituted ketones such as dihydroxyacetone, amino aldehydes, nitro aldehydes, nitro alcohols and the like. In this case, the effects induced by the use of the carbodiimide quaternary ammonium salts and the effects produced by the hardeners supplement each other and are of a synergistic nature. Thus, different properties may be obtained, or considerably lower amounts of hardening agents may be employed to achieve the desired physical properties. The reaction with formaldehyde in the presence of carbodiimide quaternary ammonium salts is believed to proceed as follows:

$$4H_2N\text{-Gel-}COOH + HCHO \longrightarrow \begin{matrix} H_2N\text{-Gel-}CONH\text{-Gel-}COOH \\ \diagdown \quad CH_2 \quad \diagup \\ H_2N\text{-Gel-}CON\text{-Gel-}COOH \end{matrix}$$

The amounts of aldehyde or other organic hardener used in this combination hardening will vary between 1 and 8 grams of aldehyde per kilogram of gelatin depending on the aldehyde chosen and the degree of hardening desired. In any event the amount of organic hardener used in combination hardening will not exceed 50 percent of that amount needed to produce the selected degree of hardening when the organic hardener is used by itself.

While the above reactions have been illustrated with respect to the carboxy and amino groups of the gelatin molecules, it should be kept in mind that these molecules contain additional functional groups such as guanidino, aliphatic or aromatic hydroxyl, mercapto or disulfide linkages which may enter new bondings in the reaction. It is, therefore, evident that the aforementioned illustrations are of an explanatory nature only and should not be construed as limiting the invention to these mechanisms.

The following examples will serve to illustrate the previously described invention, although it is to be understood that the invention is not to be limited thereto.

EXAMPLE I

A high speed negative emulsion containing about 6 percent of silver bromoiodide and 8 percent of gelatin was mixed with increasing amounts of a 2 percent aqueous solution of N,N'-di(4-diethylaminophenyl)carbodiimide methyl p-toluenesulfonate and then coated on a cellulose ester filmbase. The viscosity of the emulsion was not noticeably affected by the addition of the carbodiimide salt. Melting points were determined immediately after drying and after ten days storage at room temperature and 43 percent relative humidity.

Mg. of carbodiimide salt per g. of gel.	Melting point, ° C.	Melting point, 10 days, ° C.
0	34.7	35.1
10	40.1	41.5
20	60.1	90+
30	90+	90+

The photographic properties of the material which contained 30 milligrams of carbodiimide salt per gram of gelatin which did not melt at 90° C. were compared with the photographic properties of an unhardened emulsion and of a formaldehyde hardened emulsion. The following results were obtained:

	Fog		Speed		Contrast	
High speed negative	Fresh	Aged	Fresh	Aged	Fresh	Aged
Unhardened	0.19	0.26	110	93	1.5	1.4
Formaldehyde	0.17	0.24	93	79	1.5	1.4
Carbodiimide	0.12	0.25	135	123	1.5	1.4

It will be noted that the use of carbodiimide hardener increased the speed of this film by about twenty percent. The speed advantage was retained in the aged film. Other photographic properties were not affected. The film hardened with formaldehyde showed a speed loss of about 20 percent.

EXAMPLE II

Example I was repeated with the exception that a 2 percent solution of N-cyclohexyl-N'-(4-dimethylaminophenyl)carbodiimide ethyl p-toluenesulfonate was used in place of the N,N'-di(4-diethylaminophenyl)carbodiimide methyl p-toluenesulfonate. The following results were obtained:

Mg. carbodiimide/g. gel.	Melting point, ° C.	Melting point, 10 days, ° C.
0	34.5	34.0
15	39.7	42.9
20	60.1	90+
25	71.3	90+

The photographic results obtained were similar to those reported in Example I. Contrast and fog were essentially unchanged while the speed was noticeably increased. An emulsion hardened with formaldehyde showed loss of speed, contrast and increased fog.

EXAMPLE III

A high speed X-ray emulsion containing 8 percent gelatin was mixed with increasing amounts of a 2 percent aqueous solution of N-(tert.-butyl)-N'-(γ-dimethylaminopropyl)carbodiimide ethyl p-toluenesulfonate and then coated on filmbase. After coating, the samples were

stored over saturated K_2SO_4 solution for three days. The following results were obtained:

Mg. carbodiimide/g. gel.	Melting point, ° C.	Melting point, 3 days, ° C.
0	34.9	36.2
10	36.2	43.5
20	39.5	90+
30	40.7	90+

The photographic properties of the emulsion containing 30 mg. of carbodiimide per gram of gelatin were compared with an unhardened type and a film hardened with formaldehyde. The following results were obtained:

Table I

	Fog		Speed		Contrast	
High speed negative	Fresh	Aged	Fresh	Aged	Fresh	Aged
Unhardened type	0.10	0.16	107	110	1.7	1.4
Formaldehyde hardened	0.11	0.17	102	85	1.6	0.6
Carbodiimide hardened	0.12	0.17	120	120	1.7	1.4

The significantly improved aging behavior of the cardodiimide hardened films with respect to speed and contrast is evident.

EXAMPLE IV

Coatings were made as in Example I using both N,N'-di(4 - diethylaminophenyl)carbodiimide dimethosulfate and formaldehyde in various amounts. The following melting points were observed:

Mg. carbodiimide/g. gel.	Mg. formaldehyde/g. gel.	Melting point, ° C.	Melting point, 10 days, ° C.
0	None	34.7	35.1
10	None	40.1	41.5
None	1	37.5	38.9
None	3	37.9	39.3
None	6	41.3	52.7
10	1	39.5	45.7
10	3	40.5	62.2
10	6	50.2	90+

It will be noted from this table that the synergistic effect resulting from the combined use of formaldehyde and carbodiimide in raising the melting point of the coating is very pronounced.

EXAMPLE V

Example IV was repeated with the exception that N-cyclohexyl-N'-(4-dimethylaminophenyl)carbodiimide ethyl p-toluenesulfonate was used in place of N,N'-di(4-diethylaminophenyl)carbodiimide dimethosulfate. The following results were obtained:

Mg. carbodiimide/g. gel.	Mg. glyoxal/g. gel.	Melting point, ° C.
0	None	34.9
10	None	36.2
20	None	39.5
30	None	40.7
None	1	36.4
None	2	39.3
None	4	41.9
10	2	43.0
20	2	62.9
30	2	76.1

Thus, a level of carbodiimide which was insufficient by itself to appreciably harden the emulsion coating, was effective as a hardener when combined with a glyoxal which by itself was also incapable to appreciably harden the emulsion coatings. The photographic properties of

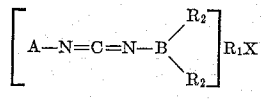
the film hardened with the combination of formaldehyde and carbodiimide were excellent. Even after extended storage, no loss of speed and contrast was observed, a positive indication that the undesirable "photographic effects of after hardening" were obviated.

Various modifications of this invention will occur to persons skilled in the art. We, therefore, do not intend to be limited in the patent granted except as necessitated by the appended claims. For instance, in place of the formaldehyde and the glyoxal illustrated by the examples, other known hardening agents can be used.

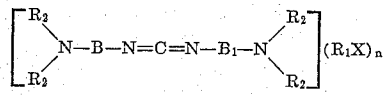
This application is a continuation-in-part of our application, Serial No. 609,529, filed September 13, 1956, now abandoned.

We claim:

1. A silver halide emulsion adapted to form a hardened layer comprising a gelatin silver halide photographic emulsion containing (*a*) a member selected from the group consisting of:

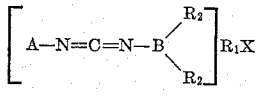


and

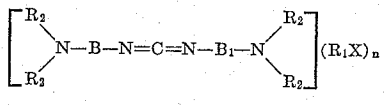


wherein A represents members selected from the group consisting of methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, tert.-butyl, allyl, crotyl, betahydroxyethyl, methoxymethyl-beta-bromoallyl, phenyl, tolyl, xylyl, naphthyl, chlorophenyl, bromophenyl, iodophenyl, cyclohexyl, bornyl, menthyl, pyridyl and quinolyl; R_1 and R_2 represent lower alkyls; B and B_1 represent members selected from the group consisting of propylene, phenylene, tolylene and propylphenylene, X is an anion selected from the group consisting of chloride, bromide, iodide, methosulfate, ethosulfate, p-toluene sulfonate and *n* is a positive integer not greater than 2, and (*b*) an organic hardener selected from the group consisting of formaldehyde, glyoxal, glycol aldehydes, diketones, mucochloric acid, mucobromic acid, formylacrylic acid, glyoxylic acid, chloroacetone, dichloroacetone, dibromoacetone, dihydroxyacetone, amino aldehydes, nitro aldehydes and nitro alcohols.

2. A composition of matter comprising a solution of gelatin containing (*a*) a member selected from the group consisting of:



and



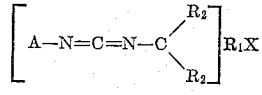
wherein A represents members selected from the group consisting of methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, tert.-butyl, allyl, crotyl, betahydroxyethyl, methoxymethyl-beta-bromoallyl, phenyl, tolyl, xylyl, naphthyl, chlorophenyl, bromophenyl, iodophenyl, cyclohexyl, bornyl, menthyl, pyridyl and quinolyl, R_1 and R_2 represent lower alkyls, B and B_1 represent members selected from the group consisting of propylene, phenylene, tolylene and propylphenylene, X is an anion selected from the group consisting of chloride, bromide, iodide, methosulfate, ethosulfate, p-toluene sulfonate and *n* is a positive integer not greater than 2, and (*b*) an organic hardener selected from the group consisting of formaldehyde, glyoxal, glycol aldehydes, diketones, mucochloric acid, mucobromic acid, formylacrylic acid, glyoxylic acid, chloroacetone, dichloroacetone, dibromoacetone, dihydroxy acetone, amino aldehydes, nitro aldehydes, and nitro alcohols.

3. A gelatin silver halide light emulsion as defined by claim 1 wherein the hardening agent of (*b*) is glyoxal.

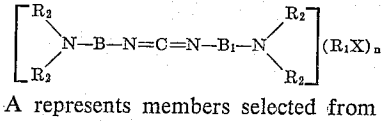
4. A gelatin silver halide light emulsion as defined by claim 1 wherein the hardening agent of (*b*) is formaldehyde.

5. A composition of matter according to claim 2 wherein the hardening agent of (*b*) is formaldehyde.

6. A method of producing a hardened gelatin silver halide emulsion layer in the photographic element which comprises uniformly mixing with an aqueous gelatin silver halide emulsion a hardening amount of (*a*) a member selected from the group consisting of:



and



wherein A represents members selected from the group consisting of methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, tert.-butyl, allyl, crotyl, beta-hydroxyethyl, methoxymethyl-beta-bromo-allyl, phenyl, tolyl, xylyl, naphthyl, chlorophenyl, bromophenyl, iodophenyl, cyclohexyl, bornyl, menthyl, pyridyl and quinolyl; R_1 and R_2 represent lower alkyls; B and B_1 represent members selected from the group consisting of propylene, phenylene, tolylene and propylphenylene, X is an anion selected from the group consisting of chloride, bromide, iodide, methosulfate, ethosulfate, p-toluene sulfonate and *n* is a positive integer not greater than 2, and (*b*) an organic hardener selected from the group consisting of formaldehyde, glyoxal, glycol aldehydes, diketones, mucochloric acid, mucobromic acid, formylacrylic acid, glyoxylic acid, chloroacetone, dichloroacetone, dibromoacetone, dihydroxy acetone, amino aldehydes, nitro aldehydes and nitro alcohols and coating said emulsion on a support and drying the layer just formed.

7. A method according to claim 6 wherein the hardener of (*b*) is formaldehyde.

8. A method according to claim 6 wherein the hardener of (*b*) is glyoxal.

9. A silver-halide emulsion as defined by claim 1, wherein said quaternary ammonium salt is N,N'-di(4-diethylaminophenyl)carbodiimide methyl p-toluenesulfonate.

10. A silver-halide emulsion as defined by claim 1, wherein said quaternary ammonium salt is N-cyclohexyl-N'-(4-dimethylaminophenyl)carbodiimide ethyl p-toluenesulfonate.

11. A silver-halide emulsion as defined by claim 1, wherein said quaternary ammonium salt is N-(tert.-butyl)-N'-(γ-dimethylaminopropyl)carbodiimide ethyl p-toluenesulfonate.

12. A composition of matter as defined by claim 1, wherein said quaternary ammonium salt is N,N'-di(4-diethylaminophenyl)carbodiimide methyl p-toluenesulfonate.

13. A composition of matter as defined by claim 1, wherein said quaternary ammonium salt is N-cyclohexyl-N'-(4-dimethylaminophenyl)carbodiimide ethyl p-toluenesulfonate.

14. A composition of matter as defined by claim 1, wherein said quaternary ammonium salt is N-(tert.-butyl) - N' - (γ - dimethylaminopropyl)carbodiimide ethyl p-toluenesulfonate.

15. A method of producing hardened silver-halide emulsion layers as defined by claim 6, wherein said quaternary ammonium salt is N,N'-di(4-diethylaminophenyl)carbodiimide methyl p-toluenesulfonate.

16. A method of producing hardened silver-halide

emulsion layers as defined by claim 6, wherein said quaternary ammonium salt is N-cyclohexyl-N'-(4-dimethylaminophenyl)carbodiimide p-toluenesulfonate.

17. A method of producing hardened silver-halide emulsion layers as defined by claim 6, wherein said quuaternary ammonium salt is N-(tert.-butyl)-N'-(γ-dimethylaminopropyl)carbodiimide ethyl p-toluenesulfonate.

References Cited in the file of this patent

UNITED STATES PATENTS

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UNITED STATES PATENT OFFICE

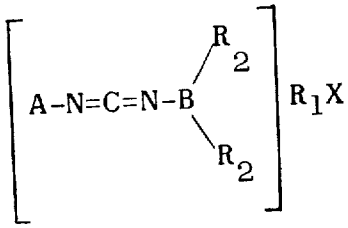
CERTIFICATE OF CORRECTION

Patent No. 3,100,704 August 13, 1963

Robert F. Coles et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 6, line 20, strike out "High speed negative"; column 8, lines 15 to 18, the formula should appear as shown below instead of as in the patent:



same column 8, lines 59, 63 and 67, for the claim reference numeral "1", each occurrence, read -- 2 --; column 9, line 6, for "quuaternary" read -- quaternary --.

Signed and sealed this 30th day of June 1964.

(SEAL)
Attest:

ERNEST W. SWIDER

Attesting Officer

EDWARD J. BRENNER

Commissioner of Patents