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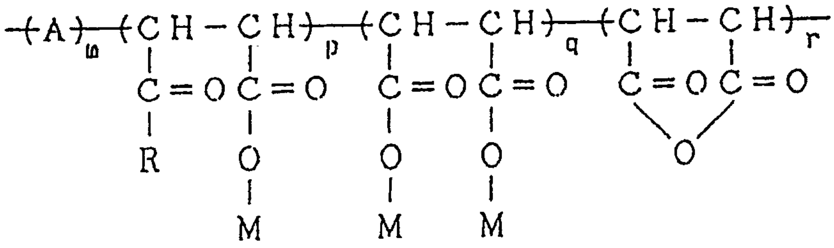
(54) Support for photographic paper.

(57) A support for a photographic paper is disclosed. The support comprises a substrate having a polyolefin resin on its surface, and, provided thereon, a subbing layer containing gelatin, a water-soluble polymeric compound represented by the following General formula and a carboxyl group reactive hardening agent;

General formula



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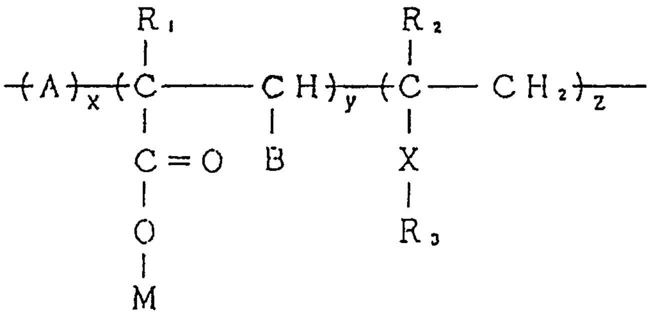


$$-(A)_x-(C(R_1)(C(=O)-O-M)-CH(B))_y-(C(R_2)(X-R_3)-CH_2)_z-$$

SUPPORT FOR PHOTOGRAPHIC PAPER

FIELD OF THE INVENTION

The present invention relates to a photographic paper support applied with a subbing treatment and having a surface improved in adhesion to an adherend and at the same time endowed with antistatic properties.

BACKGROUND OF THE INVENTION

In recent years, as photographic supports, ordinary papers have been replaced by synthetic resin films because of the latter's superiority in water resistance, smoothness and so forth. They accordingly have been used also in supports for photographic papers, but have not been satisfactory because they can not be well adhered to a light-sensitive photographic layer or an anti-curl layer provided on the back of a support and hence tend to peel. For this reason, the surface of a support is activated by a treatment such as corona discharge treatment before a light-sensitive photographic layer is formed by coating. No satisfactory results, however, have been obtained.

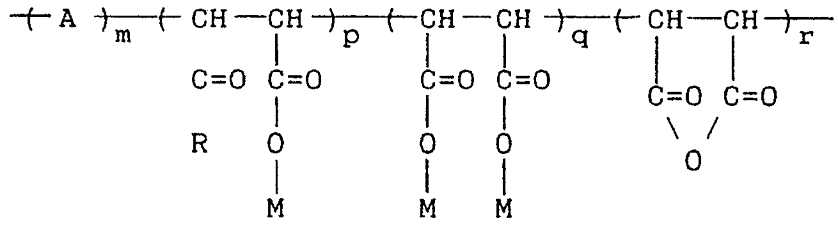
When a light-sensitive photographic material is prepared, it is very important to impart antistatic properties to its support. If this is insufficient, partial fog called static marks may occur which is undesirable from the viewpoint of photographic performance. Originally, a light-sensitive photographic material must be endowed with both the adhesion properties and the antistatic properties. However, a treatment to improve the adhesion properties and a treatment to impart the antistatic properties tend to bring about a mutual cancellation of their effects, such that the antistatic properties decrease when it is attempted to impart sufficient adhesion properties and conversely the adhesion properties decrease when it is attempted to impart sufficient antistatic properties. Thus, under the existing circumstances, no satisfactory light-sensitive photographic materials have been obtained.

SUMMARY OF THE INVENTION

The present invention was made in order to solve the above problems. Accordingly, an object of the present invention is provide a photographic paper support having a surface improved in adhesion to an adherend and at the same time endowed with antistatic properties.

The above object of the present invention can be achieved by a support for a photographic paper, comprising a substrate having a polyolefin resin on its surface, and, provided thereon, a subbing layer containing a gelatin, a water-soluble polymeric compound represented by the following General formula and a carboxyl group reactive hardening agent.

General formula:



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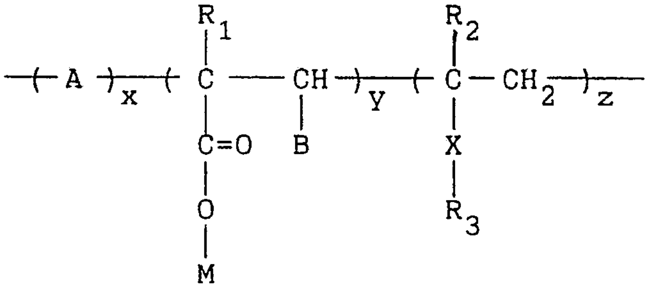
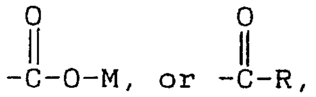
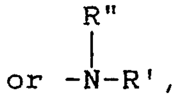


wherein A represents a vinyl monomer; B represents a hydrogen atom,



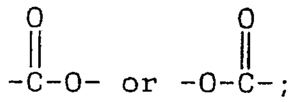
$$-\overset{O}{\overset{\|}{C}}-O-M, \text{ or } -\overset{O}{\overset{\|}{C}}-R,$$

provided that B represents a hydrogen atom when z is 0 or when R_1 is an alkyl group; M represents a hydrogen atom or a cation, provided that the cation is substituted at a rate of not less than 10 % based on all M's contained in the water-soluble polymeric compound represented by said general formula; R represents $-O-R'$,



$$\text{or } -\underset{}{\overset{R''}{\overset{|}{N}}}-R',$$

where R' represents an alkyl group, an aralkyl group, an aryl group, a heterocyolic residual group or a non-metallic atom necessary to complete a heterocyclic ring together with R''; R'' represents a hydrogen atom, a lower alkyl group or a non-metallic atom necessary to complete a heterocyclic ring together with R^1; R_1 and R_2 each represent a hvdrogen atom or a lower alkyl groups X represents



$$-\overset{O}{\overset{\|}{C}}-O- \text{ or } -O-\overset{O}{\overset{\|}{C}}-;$$

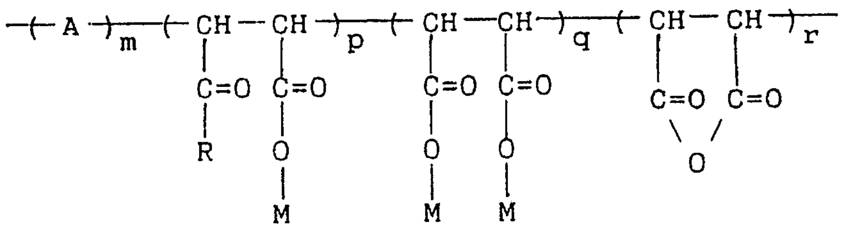
R_3 represents a halogenoalkyl group or a halogenoalkyloxyalkyl group; m, p, q, r, x, y and z each represent a value to show mol % of each monomer, where m is 40 to 60, p is 0 to 60, q is 0 to 50, r is 0 to 5, x is 0 to 70, y is 20 to 80, and z is 0 to 80, provided that $m + p + q + r = 100$ and $x + y + z = 100$.

The present invention makes it possible to provide a photographic paper support applied with a subbing treatment and having a surface improved in adhesion to an adherend and at the same time endowed with antistatic properties.

DETAILED DESCRIPTION OF THE INVENTION

The present invention will now be described below in detail.

The water-soluble polymeric compound of a specific type as used in the present invention is represented by the following general formula.



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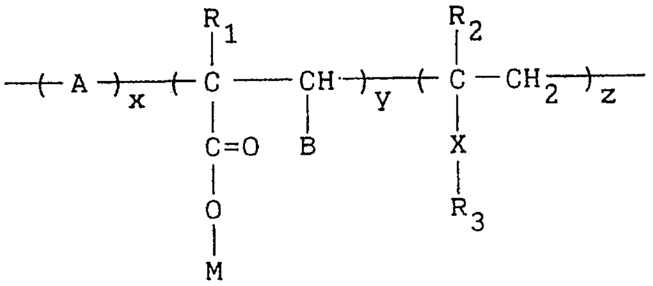
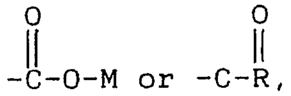


$$-(A)_x-(C(R_1)(COOM)-CH(B))_y-(C(R_2)(X-R_3)-CH_2)_z-$$

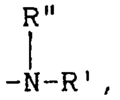
wherein A represents a vinyl monomer; B represents a hydrogen atom,



$$-\overset{O}{\overset{\|}{C}}-O-M \text{ or } -\overset{O}{\overset{\|}{C}}-R,$$

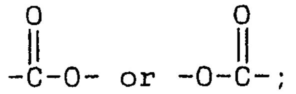
provided that B represents a hydrogen atom when z is 0 or when R_1 is an alkyl group; M represents a hydrogen atom or a cation; R represents -O-R′

or



$$-\overset{R''}{\overset{|}{N}}-R',$$

where R′ represents an alkyl group, an aralkyl group, an aryl group, a heterocyclic residual group or a non-metallic atom necessary to complete a heterocyclic ring together with R"; R" represents a hydrogen atom, a lower alkyl group or a non-metallic atom necessary to complete a heterocyclic ring together with R′; R_1 and R_2 each represent a hydrogen atom or a lower alkyl group; X represents

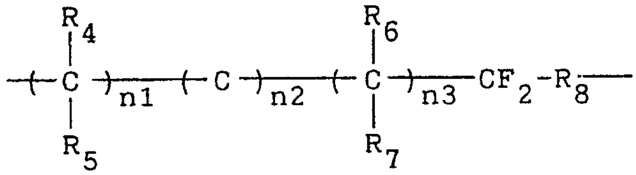


$$-\overset{O}{\overset{\|}{C}}-O- \text{ or } -O-\overset{O}{\overset{\|}{C}}-;$$

R_3 represents a halogenoalkyl group or a halogenoalkyloxyalkyl group; m, p, q, r, x, y and z each represent a value to show mol % of each monomer, where m is 40 to 60, p is 0 to 60, q is 0 to 50, r is 0 to 5, x is 0 to 70, y is 20 to 80, and z is 0 to 80, provided that m + p + q + r = 100 and x + y + z = 100.

In the above general formula, the vinyl monomer includes, for example, styrene, a styrene substituted with a nitro group, a fluorine atom, a chlorine atom, a bromine atom, a chloromethyl group or a lower alkyl group, vinyl methyl ether, vinyl ethyl ether, vinyl chloroethyl ether, vinyl acetate, vinyl chloroacetate, vinyl propionate, an unsaturated acid such as acrylic acid, methacrylic acid or itaconic acid, an alkyl acrylate or alkyl methacrylate in which the alkyl moiety has 1 to 5 carbon atoms and is unsubstituted or substituted with a chlorine atom or a phenyl group, phenyl acrylate or phenyl methacrylate, acrylonitrile, vinyl chloride, vinylidene chloride, ethylene, acrylamide, an acrylamide substituted with an alkyl group having 1 to 5 carbon atoms, a chlorine atom or a phenyl group, vinyl alcohol, glycidyl acrylate, and acrolein. Preferred are styrene, a styrene having a substituent, vinyl acetate, vinyl methyl ether, an alkyl acrylate, acrylonitrile. etc.

The alkyl group represented by R' in the above formula may preferably be an alkyl group having 1 to 24 carbon atoms, and may be any alkyl group including a straight-chain alkyl group, a branched alkyl group and a cycloalkyl group. This alkyl group may also have a substitutent, and such a substituent includes a hydroxyl group, a hydroxycarbonyl group, a cationic oxycarbonyl group. In particular, desired results can be obtained when it is a halogenoalkyl group or halogenoalkyloxyalkyl group substituted with a halogen atom such as a fluorine atom, herein including a halogenoalkyl group, halogenoalkyloxyalkyl group or halogenocycloalkyl group having 2 to 18 carbon atoms. The number of the halogen atom should be 1 to 37. This halogenoalkyl group or halogenoalkyloxyalkyl group and the halogenoalkyl group or halogenoalkyloxyalkyl group represented by R_3 in the above formula may preferably be represented by the following Formula A.



$$-\left(\overset{R_4}{\underset{R_5}{C}}\right)_{n1}-\left(C\right)_{n2}-\left(\overset{R_6}{\underset{R_7}{C}}\right)_{n3}-CF_2-R_8-$$

wherein R_4, R_5, R_6, R_7 and R_8 each represent a hydrogen atom or a fluorine atom; n_2 is 0 or 1, n_1 is 0 when n_2 is 0, n_1 is 2 or 3 when n_2 is 1, and n_3 is an integer of 1 to 17, provided that $n_1 + n_3$ is 1 to 17; when R_4 is present in the number of two or more in the structural formula, they may be different atoms such that one of them is a hydrogen atom and the other of them is fluorine atom; and, when R_5, R_6 and R_7 are each present in a plural number in the structural formula, they may be atoms different from each other.

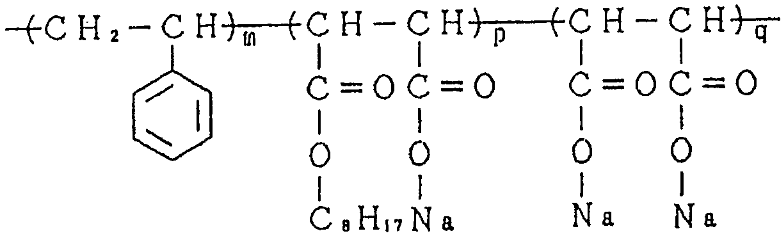
When R' in the above general formula is such a halogenoalkyl group or halogenoalkyloxyalkyl group, R in the above general formula should preferably be $-O-R'$. The aryl group represented by R', such as a phenyl group, or the aralkyl group such as a benzyl group may also have a substituent. Such a substitutent includes a halogen atom such as fluorine, chlorine or bromine, a lower alkyl group, a hydroxyl group, a hydroxycarbonyl group, a cationic oxycarbonyl group, a nitrile group and a nitro group. The heterocyclic ring represented by R' in the formula or the heterocyclic ring formed by R' and R'' may be a saturated or unsaturated heterooyclic ring containing an oxygen atom, a sulfur atom or a nitrogen atom, which is a heterocyclic ring selected from heterocyclic rings as exemplified by azilidine, pyrol, pyrolidine, pyrazole. imidazole, imidazoline, triazole, piperidine, piperazine. oxazine, morpholine, and thiazine. The cation represented by M in the formula includes cations as exemplified by an ammonium ion, a sodium ion, a potassium ion and a lithium ion. The cation should preferably be substituted at a rate of not less than 10 % based on all M's contained in the water-soluble polymeric compound.

The water-soluble polymeric compound represented by the above general formula may be used alone or in combination of two or more kinds. It is prefered to use a water-soluble polymeric compound having an average molecular weight of about 500 to about 500,000.

The water-soluble polymeric compound used in the present invention may typically include the following compounds.

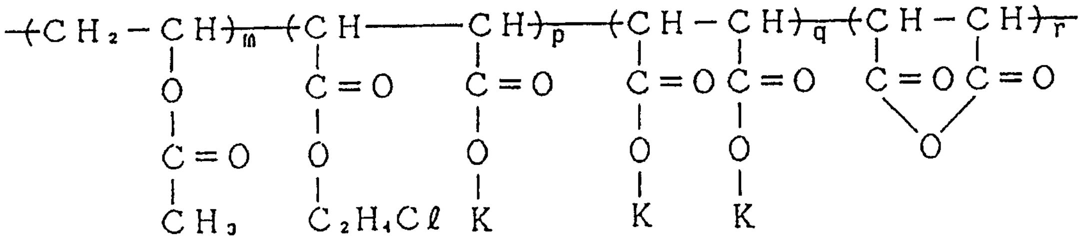
Exemplary Compounds:

(1)



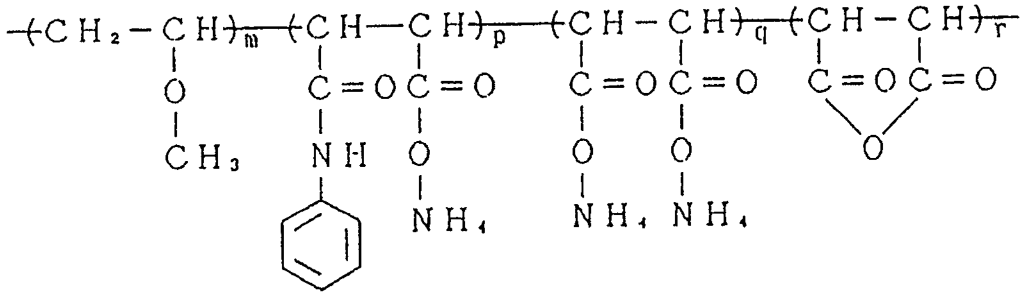
(m=45, p=35, q=20)

(2)



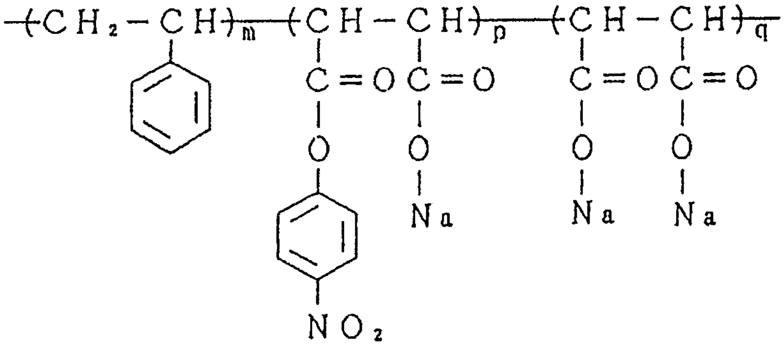
(m=50, p=30, q=15, r=5)

(3)



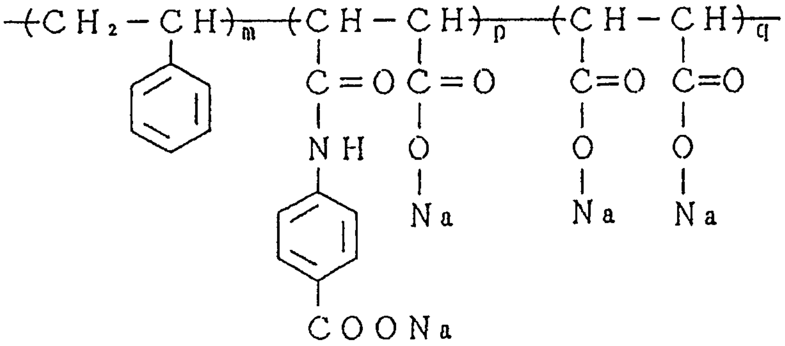
(m=55, p=20, q=20, r=5)

(4)



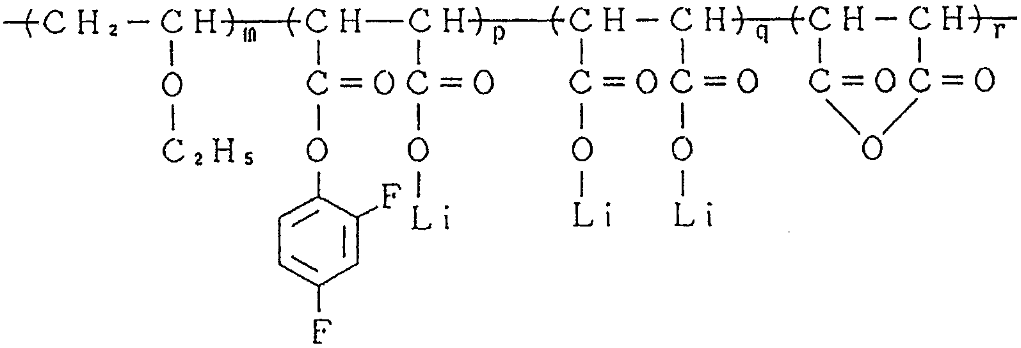
(m=50, p=20, q=30)

(5)



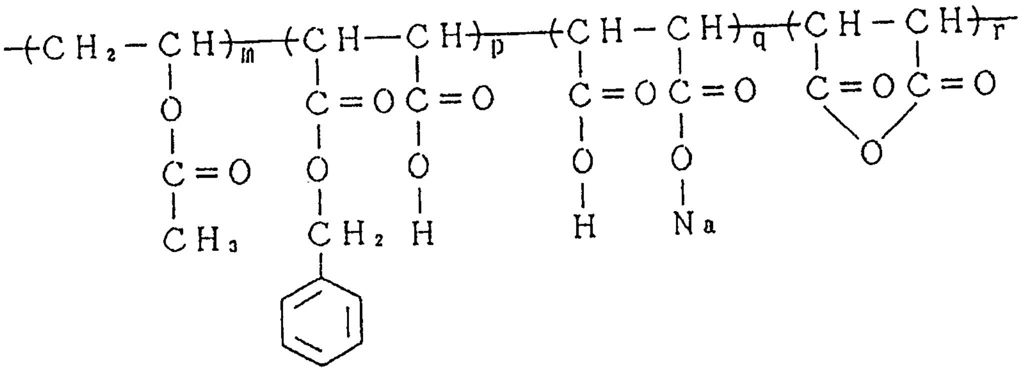
(m=50, p=30, q=20)

(6)



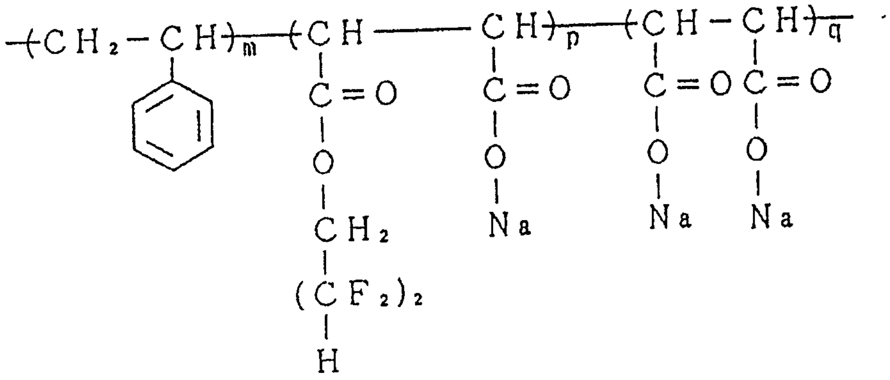
(m=40, p=30, q=25, r=5)

(7)



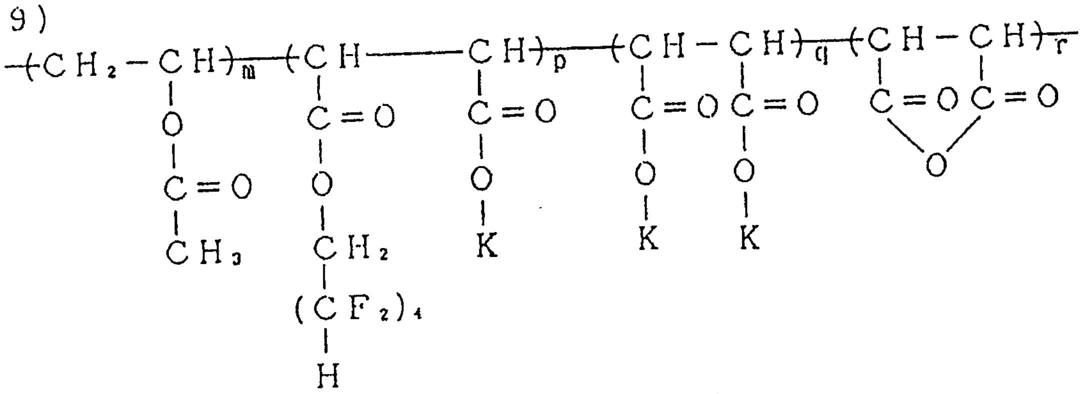
($m=50$, $p=35$, $q=10$, $r=5$)

(8)



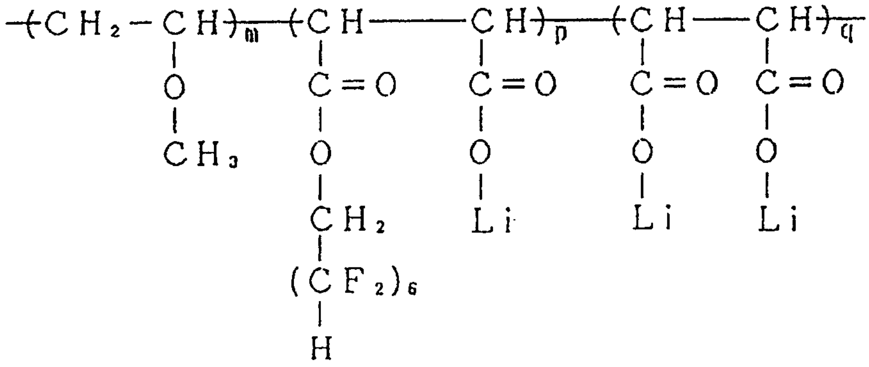
($m=50$, $p=20$, $q=30$)

(9)



($m=40$, $p=35$, $q=20$, $r=5$)

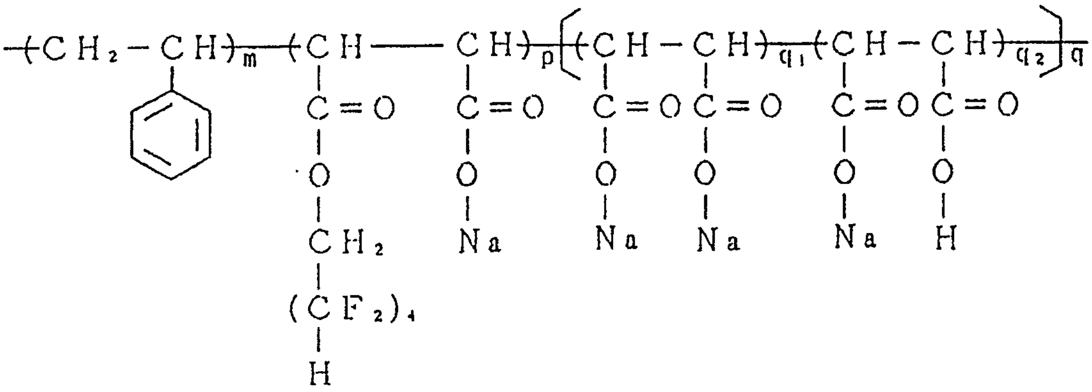
(10)



$$\left(CH_2-\underset{OCH_3}{CH}\right)_m\left(\underset{COOCH_2(CF_2)_6H}{CH}-\underset{COOLi}{CH}\right)_p\left(\underset{COOLi}{CH}-\underset{COOLi}{CH}\right)_q$$

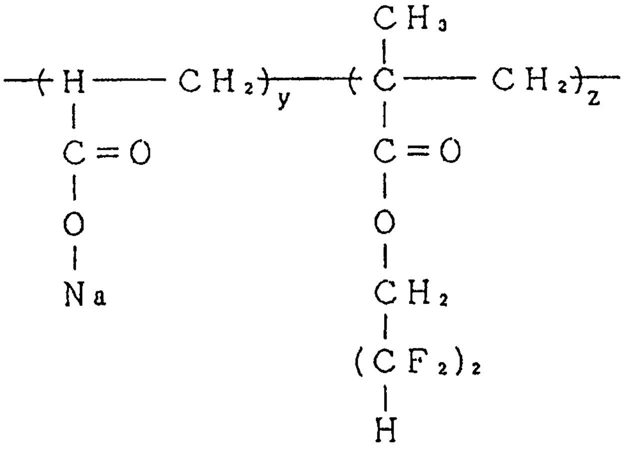
$(m=55,\ p=20,\ q=25)$

(11)



$(m=50,\ p=20,\ q=q_1+q_2,\ q_1=20,\ q_2=10)$

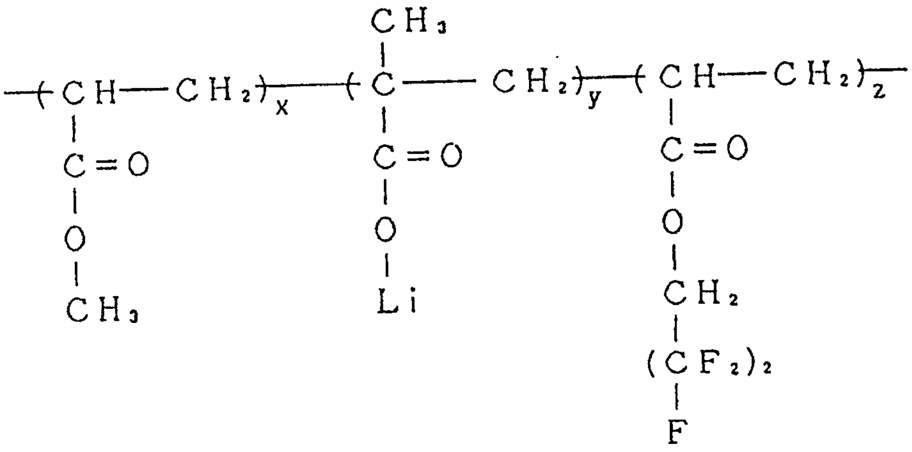
(12)



$$\left(\underset{COONa}{CH}-CH_2\right)_y\left(\overset{CH_3}{\underset{COOCH_2(CF_2)_2H}{C}}-CH_2\right)_z$$

$(y=70,\ z=30)$

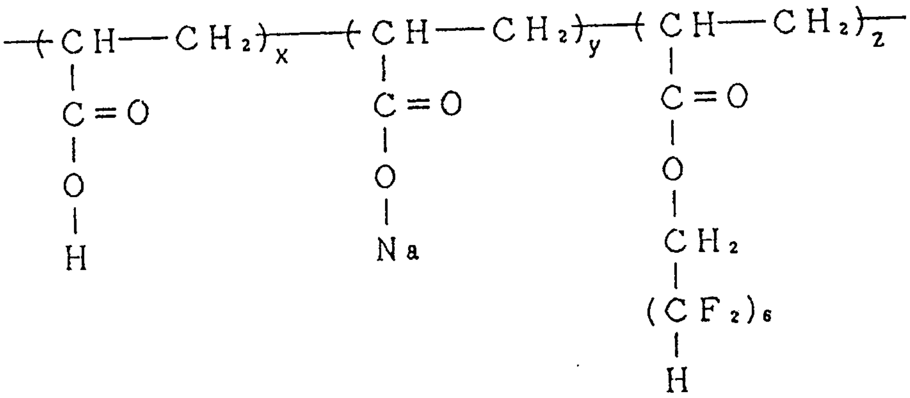
(13)



$$-\!\left(CH(COOCH_3)-CH_2\right)_x\!-\!\left(C(CH_3)(COOLi)-CH_2\right)_y\!-\!\left(CH(COOCH_2(CF_2)_2F)-CH_2\right)_z\!-$$

$(x=10,\quad y=60,\quad z=30)$

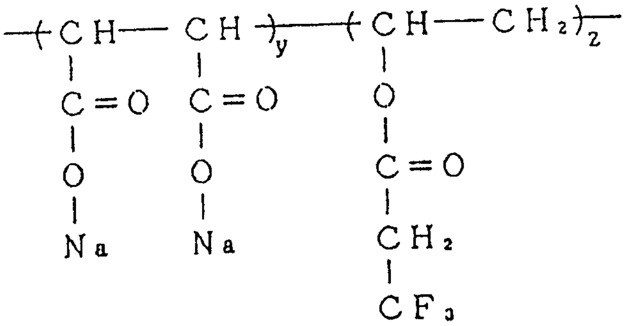
(14)



$$-\!\left(CH(COOH)-CH_2\right)_x\!-\!\left(CH(COONa)-CH_2\right)_y\!-\!\left(CH(COOCH_2(CF_2)_6H)-CH_2\right)_z\!-$$

$(x=10,\quad y=60,\quad z=30)$

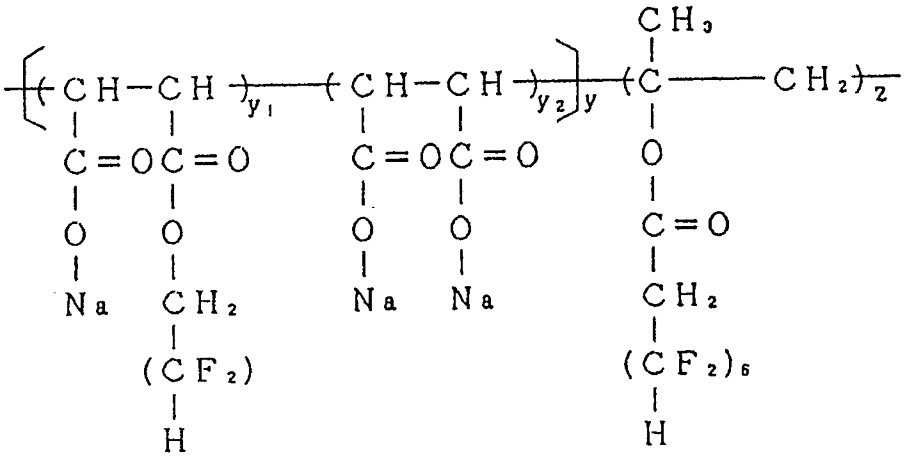
(15)



$$-\!\left(CH(COONa)-CH(COONa)\right)_y\!-\!\left(CH(OCOCH_2CF_3)-CH_2\right)_z\!-$$

$(y=55,\quad x=45)$

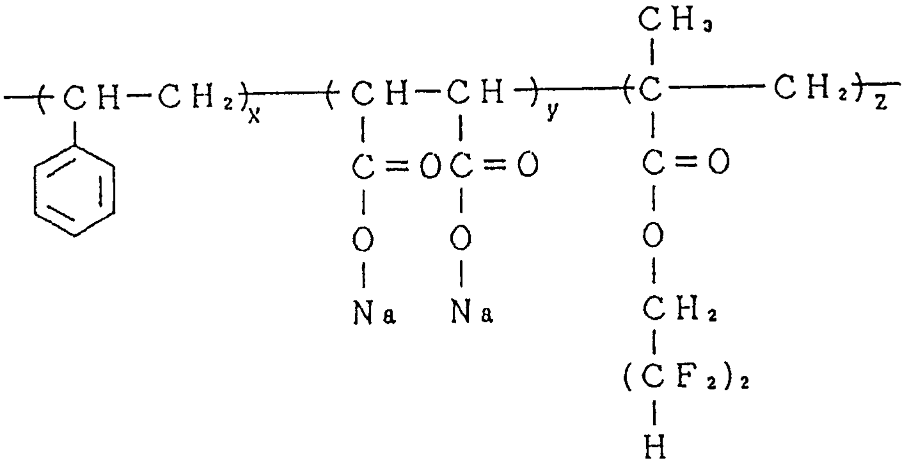
(16)



$$-\left[\left(CH(COONa)-CH(COOCH_2(CF_2)H)\right)_{y_1}-\left(CH(COONa)-CH(COONa)\right)_{y_2}\right]_y-\left(C(CH_3)(OCOCH_2(CF_2)_6H)-CH_2\right)_z-$$

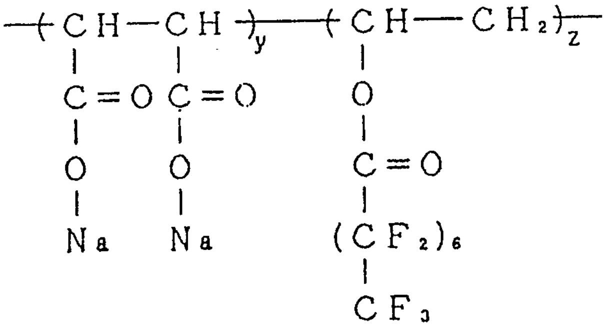
$(y=y_1+y_2,\ \ y_1=20,\ \ y_2=40,\ \ z=40)$

(17)



$(x=40,\ \ y=40,\ \ z=20)$

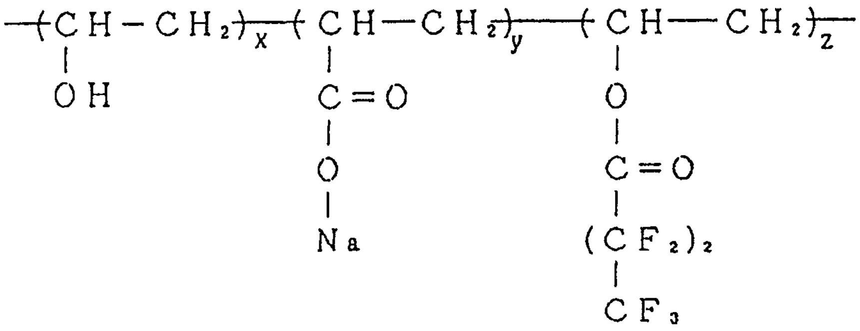
(18)



$$-\left(CH(COONa)-CH(COONa)\right)_y-\left(CH(OCO(CF_2)_6CF_3)-CH_2\right)_z-$$

$(y=50,\ \ z=50)$

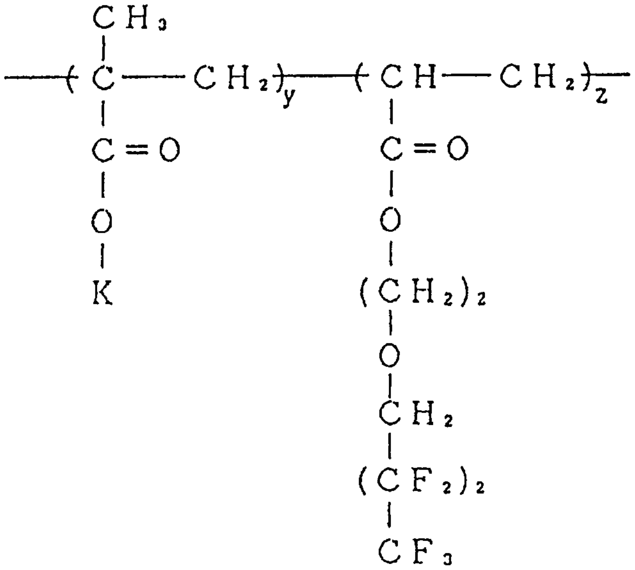
(19)



$$-(\underset{OH}{CH}-CH_2)_x-(\underset{C(=O)-O-Na}{CH}-CH_2)_y-(\underset{O-C(=O)-(CF_2)_2-CF_3}{CH}-CH_2)_z-$$

(x=15, y=45, z=40)

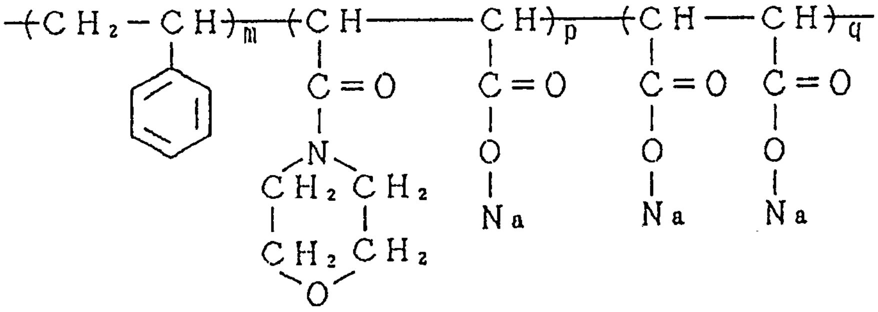
(20)



$$-(\overset{CH_3}{\underset{C(=O)-O-K}{C}}-CH_2)_y-(\underset{C(=O)-O-(CH_2)_2-O-CH_2-(CF_2)_2-CF_3}{CH}-CH_2)_z-$$

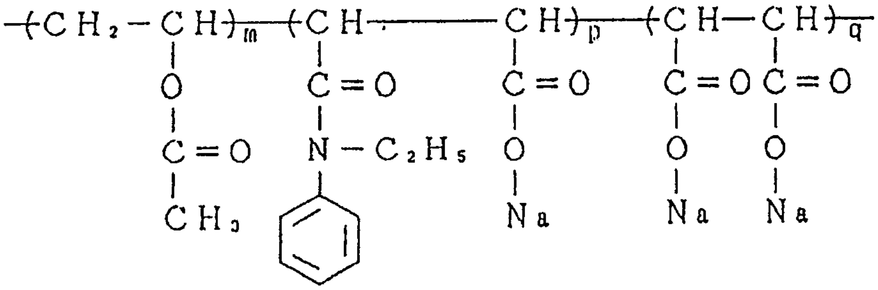
(y=60, z=40)

(21)



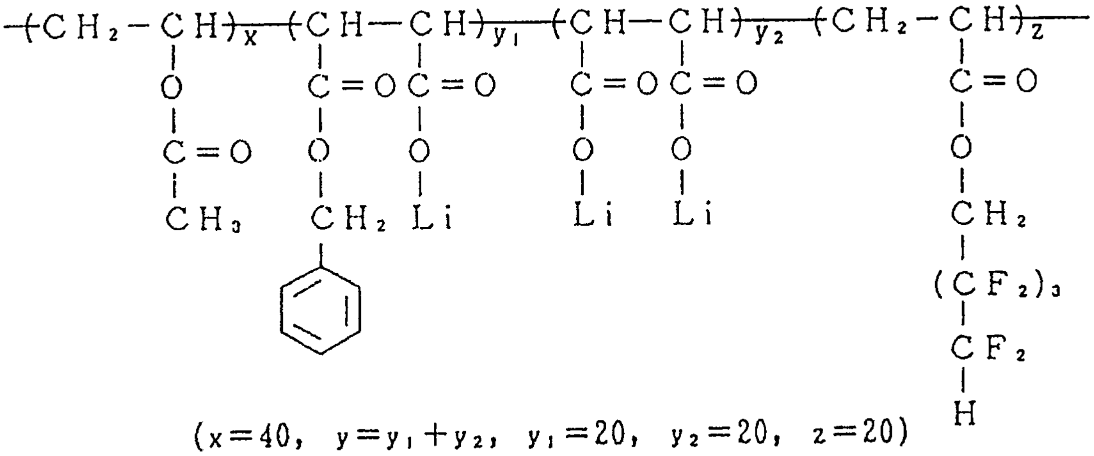
(m=40, p=40, q=20)

(22)



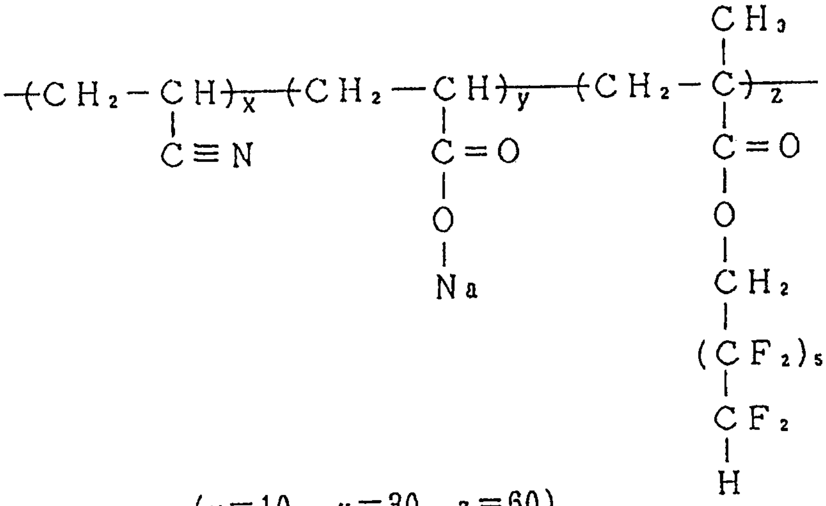
(m=40, p=50, q=10)

(23)



($x=40$, $y=y_1+y_2$, $y_1=20$, $y_2=20$, $z=20$)

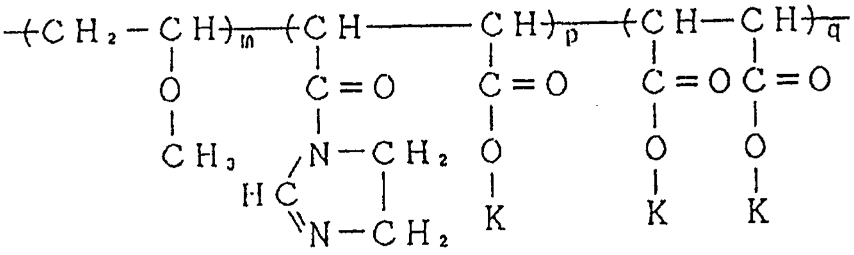
(24)



$$-\!(CH_2-CH(C\equiv N))_x\!-\!(CH_2-CH(C(=O)-O-Na))_y\!-\!(CH_2-C(CH_3)(C(=O)-O-CH_2-(CF_2)_5-CF_2-H))_z\!-$$

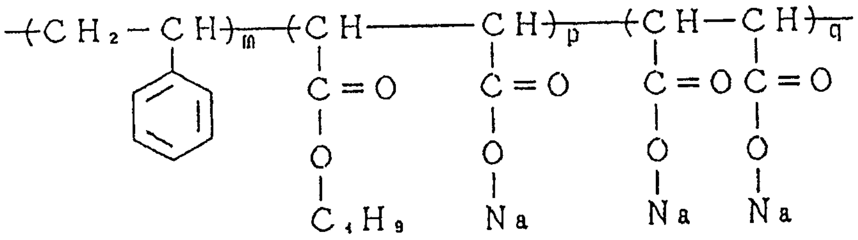
$(x=10,\ y=30,\ z=60)$

(25)



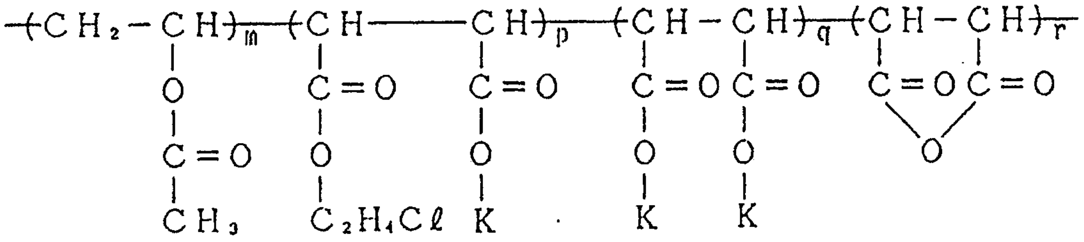
$(m=40,\ p=50,\ q=10)$

(26)



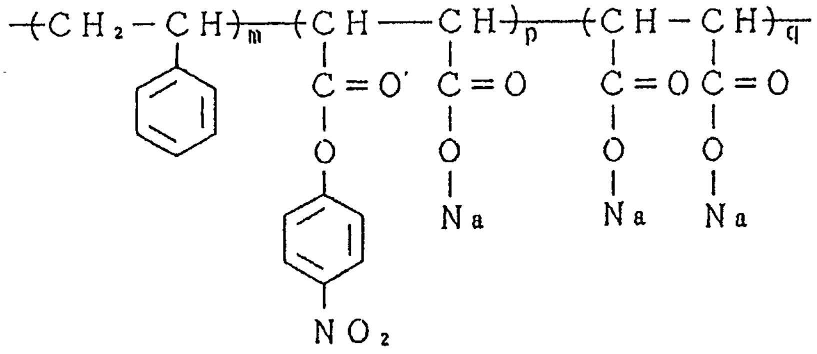
$(m=50,\ p=2,\ q=48)$

(27)



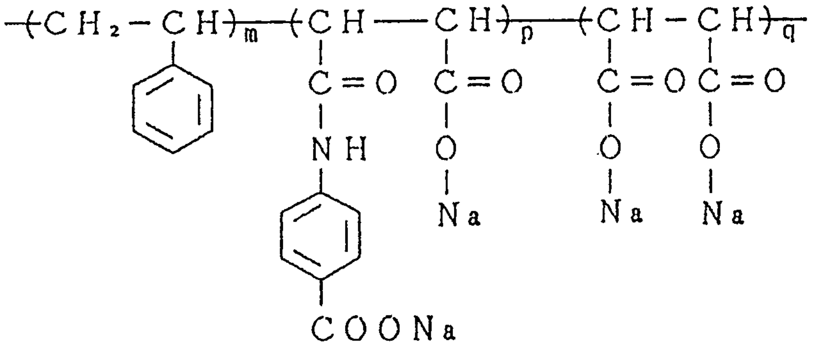
($m=40$, $p=8$, $q=47$, $r=5$)

(28)



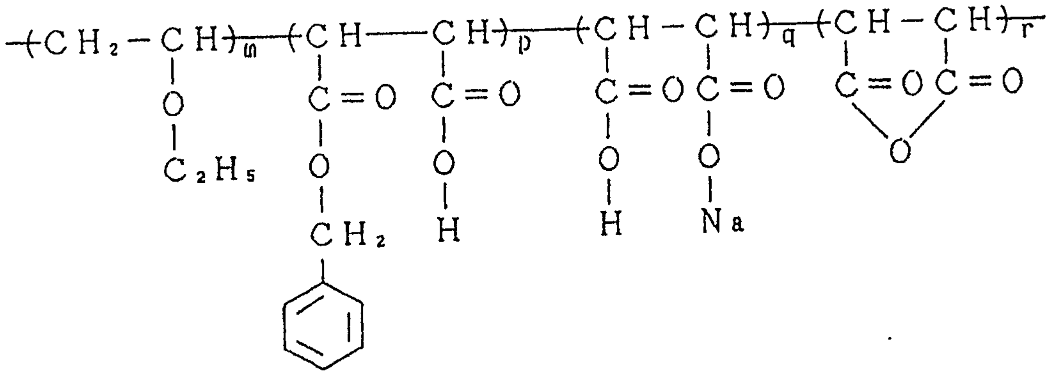
($m=50$, $p=1$, $q=49$)

(29)



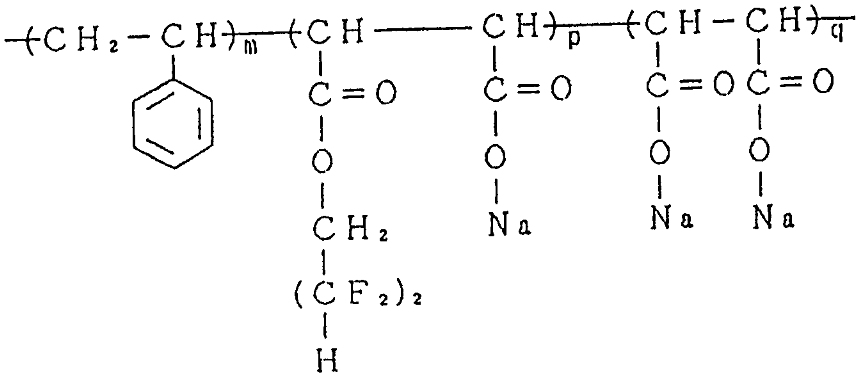
($m=50$, $p=7$, $q=43$)

(30)



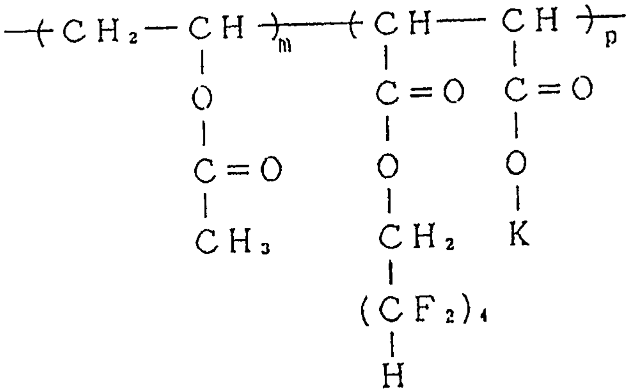
(m=50, p=9, q=36, r=5)

(31)



(m=50, p=8, q=42)

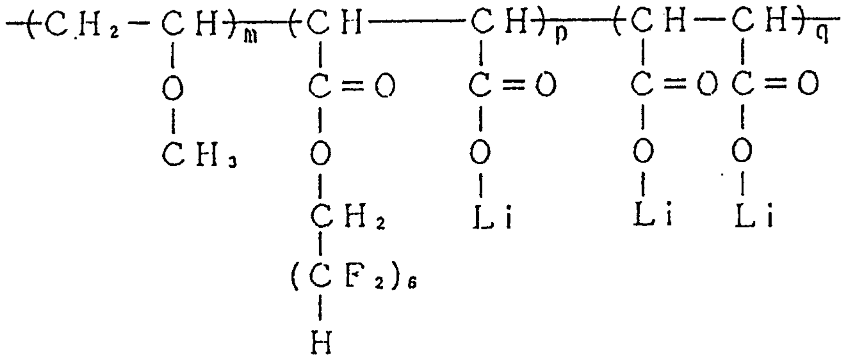
(32)



$$-\!\left(CH_2-CH(OC(=O)CH_3)\right)_m\!-\!\left(CH(C(=O)OCH_2(CF_2)_4H)-CH(C(=O)OK)\right)_p\!-$$

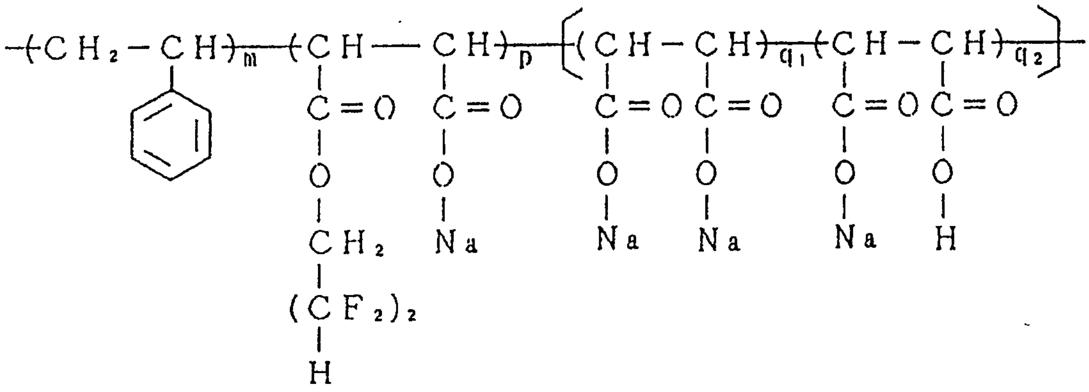
(m=40, p=60)

(33)



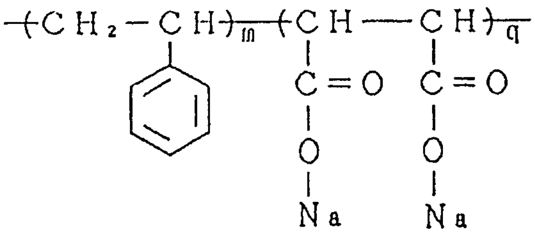
(m=55, p=2, q=43)

(34)



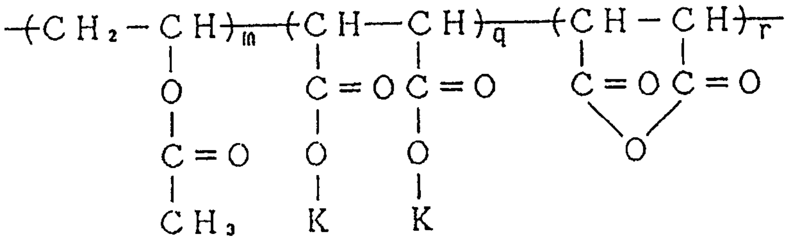
(m=50, p=7, $q_1+q_2=q$, $q_1=33$, $q_2=10$)

(35)



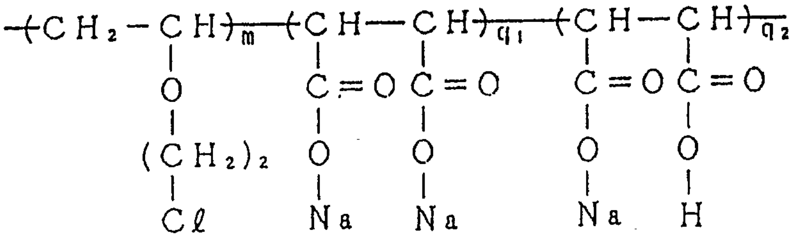
(m=50, q=50)

(36)



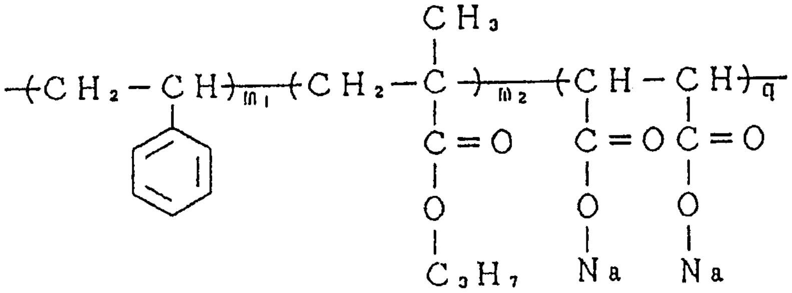
$(m=40,\ q=58,\ r=2)$

(37)



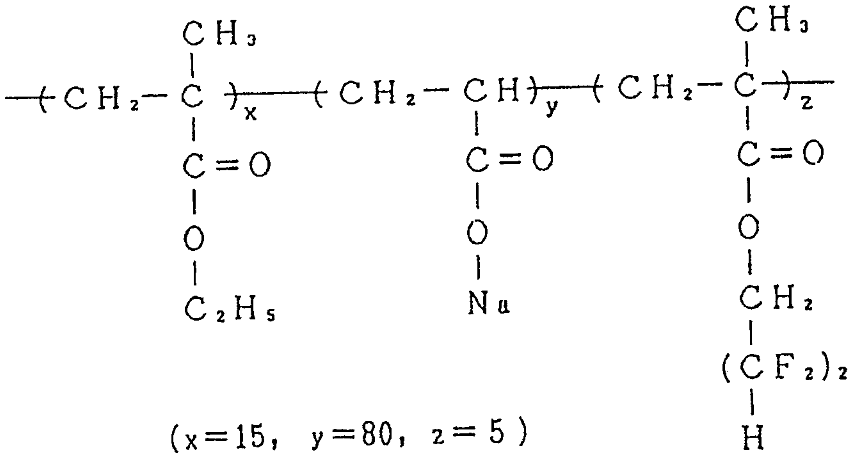
$(m=45,\ q_1+q_2=q,\ q_1=50,\ q_2=5)$

(38)



$(m_1+m_2=m,\ m_1=40,\ m_2=20,\ q=40)$

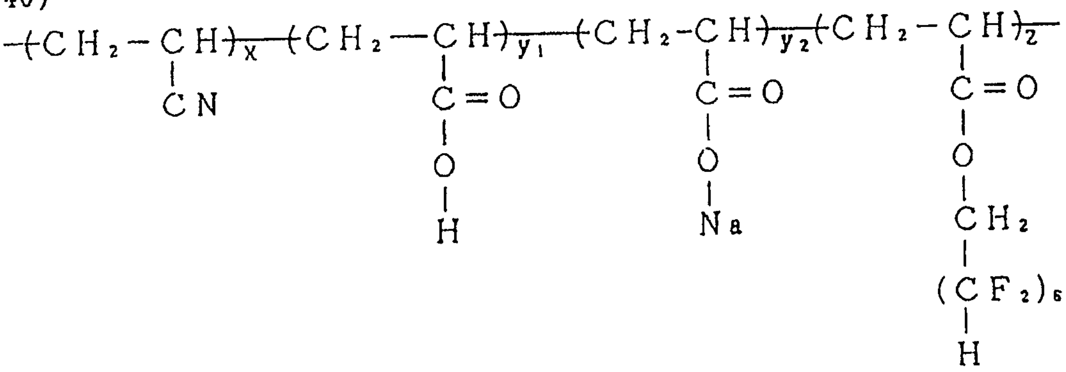
(39)



$$-(CH_2-C(CH_3)(COOC_2H_5))_x-(CH_2-CH(COONa))_y-(CH_2-C(CH_3)(COOCH_2(CF_2)_2H))_z-$$

$(x=15,\ y=80,\ z=5)$

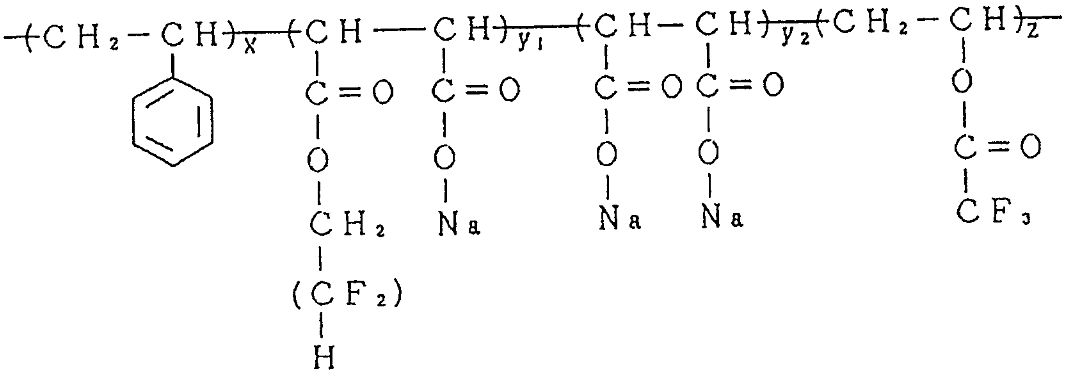
(40)



$$-(CH_2-CH(CN))_x-(CH_2-CH(COOH))_{y_1}-(CH_2-CH(COONa))_{y_2}-(CH_2-CH(COOCH_2(CF_2)_6H))_z-$$

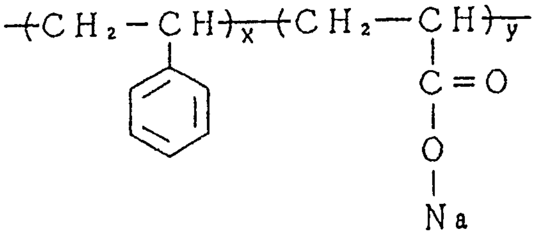
$(x=45,\ y_1+y_2=y,\ y_1=10,\ y_2=40,\ z=5)$

(41)



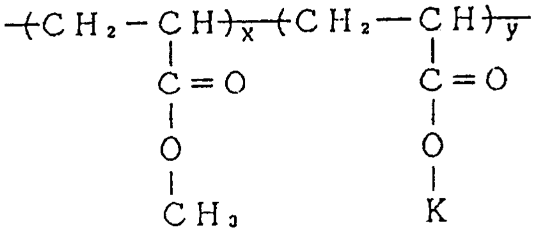
$(x=50,\ y_1+y_2=y,\ y_1=30,\ y_2=18,\ z=2)$

(42)



(x=30, y=70)

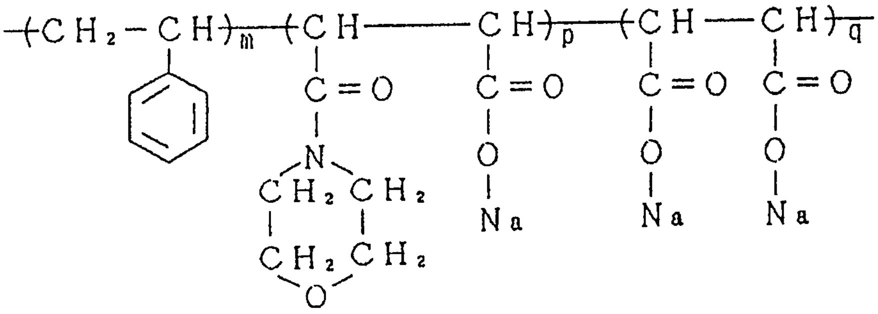
(43)



$$-\!\left(CH_2-\underset{\substack{|\\ C=O\\ |\\ O\\ |\\ CH_3}}{C}H\right)_x\!-\!\left(CH_2-\underset{\substack{|\\ C=O\\ |\\ O\\ |\\ K}}{C}H\right)_y\!-$$

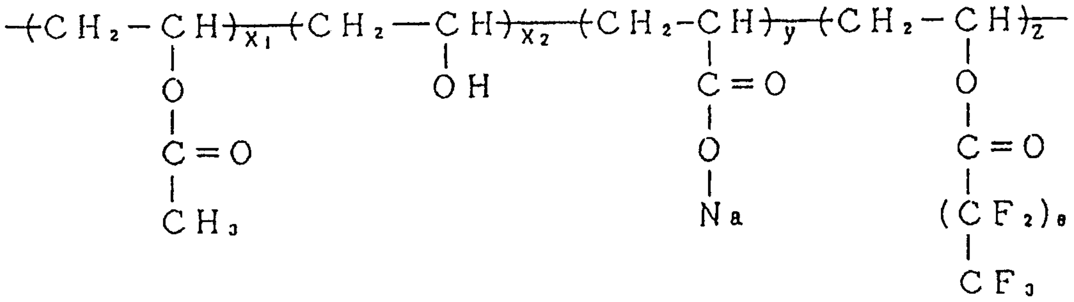
(x=42, y=58)

(44)



(m=55, p=2, q=43)

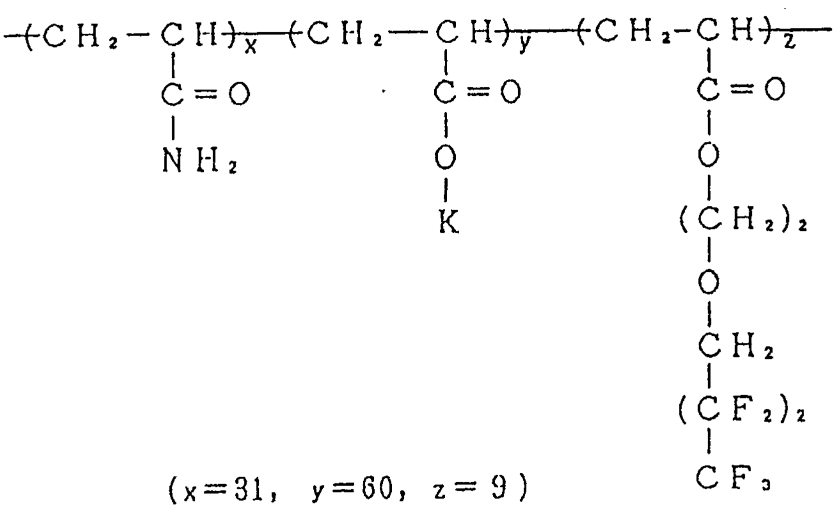
(45)



$$-(CH_2-CH(OCOCH_3))_{x_1}-(CH_2-CH(OH))_{x_2}-(CH_2-CH(COONa))_{y}-(CH_2-CH(OCO(CF_2)_8CF_3))_{z}-$$

($x_1+x_2=x$, $x_1=16$, $x_2=35$, $y=45$, $z=4$)

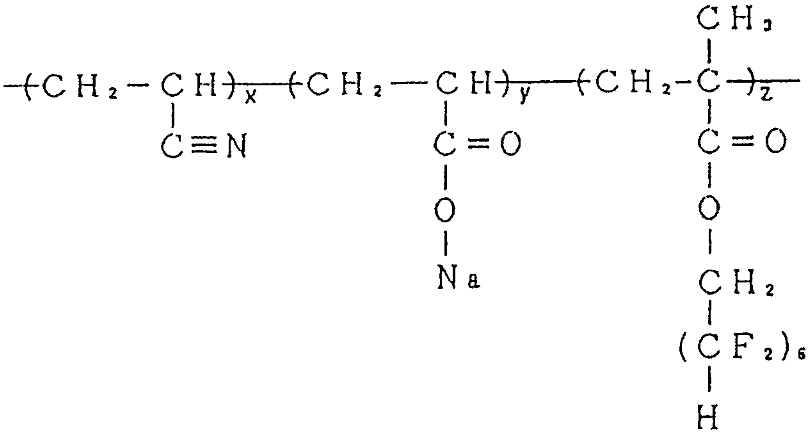
(46)



$$-(CH_2-CH(CONH_2))_{x}-(CH_2-CH(COOK))_{y}-(CH_2-CH(COO(CH_2)_2OCH_2(CF_2)_2CF_3))_{z}-$$

($x=31$, $y=60$, $z=9$)

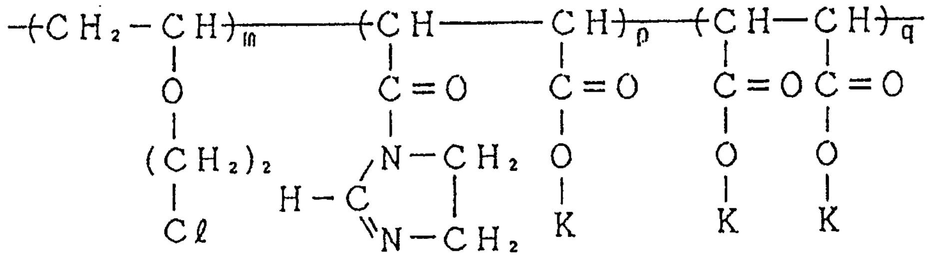
(47)



$$-(CH_2-CH(C{\equiv}N))_{x}-(CH_2-CH(COONa))_{y}-(CH_2-C(CH_3)(COOCH_2(CF_2)_6H))_{z}-$$

($x=27$, $y=70$, $z=3$)

(48)



(m=45, p= 5 , q=50)

The water-soluble polymeric compound used in the present invention, represented by the general formula, can be synthesized by a conventional method. Namely, maleic anhydride copolymers are well known to be very commonly available polymers, and hence a derivative thereof can also be readily obtained by allowing an alcohol or amine suited therefor to react with a maleic anhydride copolymer. It can also be obtained by subjecting a purified product of the reaction product of an alcohol or amine with a maleic anhydride monomer to copolymerization with a different vinyl monomer. The acrylates of the halogenoalkyl or halogenoalkyloxyalkyl can also be readily synthesized by the method of synthesizing monomers and polymers, as disclosed in Journal of Polymer Science, 15 , 515-574 (1955) or British Patent No. 1,121,357.

According to the present invention, the subbing layer contains gelatin, a water-soluble polymeric compound previously described and a carboxyl group reactive hardening agent, and the weight ratio of the water-soluble polymeric compound to the gelatin preferably ranges from 0.1 to 5.0.

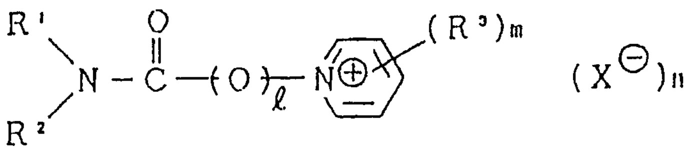
In the present invention, the water-soluble polymeric compound may preferably be used in an amount of from 10 to 800 mg/m^2, and particularly preferably from 30 to 400 mg/m^2.

A hardening agent showing a reactivity with a carboxyl group will be described below in detail.

The hardening agent showing a reactivity with a carboxyl group (hereinafter "carboxyl group reactive hardening agent") refers to a hardening agent capable of reacting with a carboxyl group contained in a binder.

The carboxyl group reactive hardening agent in the present invention includes, for example, the compounds represent by the following Formulas H-I to H-X.

Formula H-I



In the formula, R^1 and R^2 each represent an alkyl group as exemplified by a methyl group, an ethyl group, a benzyl group, a phenethyl group or a 2-ethylhexyl group, or an aryl group as exemplified by a phenyl group or a naphthyl group, and may preferably combine to form a heterocyclic ring together with a nitrogen atom. Examples of the heterocyclic ring are a pyrrolidine ring, a piperazine ring, a morpholine ring, etc.

R^3 represents a substituent as exemplified by -NR^{4}R^5 (R^4 and R^5 have the same definitions as R^1 and R^2), a halogen atom, a carbamoyl group, a sulfo group, a ureido group, an alkoxy group, or an alkyl group. R^3 includes those having a substituent, and examples of the substituent are a halogen atom, an alkyl group, a carbamoyl group, a sulfo group, a sulfoxy group and a ureido group.

The letter symbol m represents 0 to 5. When m ≧ 2, a plural number of R^3 may be the same or different from each other.

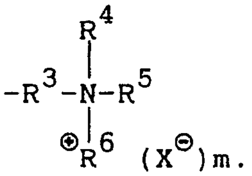
X$^\ominus$ represents an anion. Preferred examples thereof are a halide ion, a sulfate ion. a sulfonate ion,

$C10_4^{\ominus}$. $BF_4^{\ominus}$, $PF_6^{\ominus}$ etc. ℓ represents 0 or 1, and n represents 0 to 2. When an intramolecular salt is formed, n is 0.

Formula H-II

$R^1\text{-}N=C=N\text{-}R^2$

In the formula, R^1 and R^2 each represents a cycloalkyl group as exemplified by a cyclohexyl group, or an alkyl group as exemplified by a methyl group, an ethyl group or a 2-ethylhexyl group. It alternatively represents an alkoxyalkyl group such as a methoxyethyl group, an aralkyl group such as a benzyl group or a phenethyl group, or a group represented by

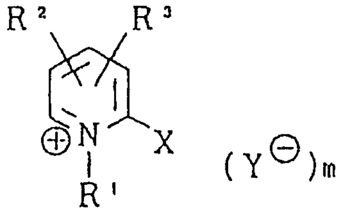


$$-R^3-\overset{\displaystyle R^4}{\underset{\displaystyle {}^{\oplus}R^6}{N}}-R^5 \quad (X^{\ominus})m.$$

Here, R^3 represents an alkylene group as exemplified by an ethylene group, a propylene group or a trimethylene group; and R^4, R^5 and R^6 each represent an alkyl group as exemplified by a methyl group or an ethyl group, including an instance in which two of R^4 to R^6 combine to form a heterocyclic ring together with a nitrogen atom, as exemplified by a pyrrolidine ring, a piperazine ring or a morpholine ring and an instance in which these groups each have a substituent.

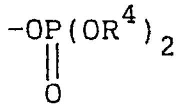
Preferred examples of such a substituent are a carbamoyl group such as diethyl carbamoyl or piperidinocarbonyl, and a sulfo group. m represents 0 or 1. $X^{\ominus}$ represents an anion, preferably including a halide ion, a sulfonate ion, a sulfate ion, $C10_4^{\ominus}$, $BF_4^{\ominus}$ and $PF_6^{\ominus}$. When an intramolecular salt is formed, m represents 0.

Formula H-III



In the formula, R^1 represents an alkyl group as exemplified by a methyl group. an ethyl group or a butyl group, an aralkyl group as exemplified by a benzyl group or a phenethyl group, or an aryl group as exemplified by a phenyl group or a naphthyl group. These groups also include those having a substituent, and examples of the substituent are a carbamoyl group, a sulfamoyl group, a sulfo group, etc. R^2 and R^3 each represent a hydrogen atom, or a substituent as exemplified by a halogen atom, an acylamido group, a nitro group, a carbamoyl group, a ureido group, an alkoxy group, an alkyl group, an alkenyl group, an aryl group or an aralkyl group. R^2 and R^3 may preferably combine to form a heterocyclic ring together with a pyridinium ring skeleton.

X represents a group capable of being split off upon reaction of the compound represented by Formula H-III, with a nucleophilic reagent. Preferred examples thereof are a halogen atom, a sulfonyloxy group, a sulfoalkyl group, and a group represented by



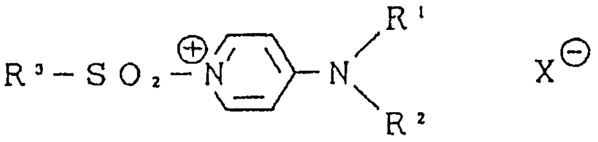
$$-O\underset{\displaystyle \overset{\|}{O}}{P}(OR^4)_2,$$

where R^4 represents an alkyl group or an aryl group.

When X represents a sulfonyloxy group, X and R^1 may preferably combine.

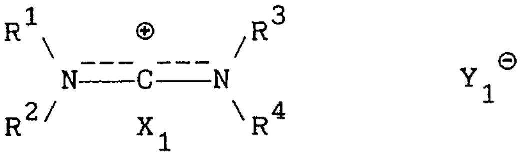
$Y^{\ominus}$ represents an anion, preferably including a halide ion, a sulfonate ion, a sulfate ion, $C10_4^{\ominus}$, $BF_4^{\ominus}$ and $PF_6^{\ominus}$. m represents 0 or 1. When an intramolecular salt is formed, m represents 0.

Formula H-IV



In the formula, R^1 and R^2 have entirely the same definitions as those for R^1 and R^2 in Formula H-I. R^3 represents an alkyl group as exemplified by a methyl group, an ethyl group or a butyl group, an aralkyl group as exemplified by a benzyl group or a phenethyl group, or an aryl group as exemplified by a phenyl group or a naphthyl group. $X^{\ominus}$ represents an anion, preferably including a halide ion, a sulfonate ion, a sulfate ion, $C10_4^{\ominus}$, $BF_4^{\ominus}$ and $PF_6^{\ominus}$.

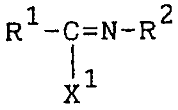
Formula H-V



In the formula, R^1 and R^2, and R^3 and R^4, each have entirely the same definitions as those for R^1 and R^2 in Formula H-I. R^1 and R^3 may further combine to form a ring.

X_1 represents a group capable of being split off upon reaction with a nucleophilic reagent, preferably including a halogen atom, a sulfonyloxy group, preferably alkylsulfonyloxy or arylsulfonyloxy, a 1-pyridium group, an imidyloxy group as exemplified by phthalimdyloxy, succinimidyloxy or glutalimidyloxy, an azolyloxy group, and an ammonio group. $Y_1^{\ominus}$ represents an anion, and preferably includes a halide ion, a sulfonate ion, a sulfate ion, $C10_4^{\ominus}$, $BF_4^{\ominus}$, $PF_6^{\ominus}$, a phosphonate ion and a phosphate ion.

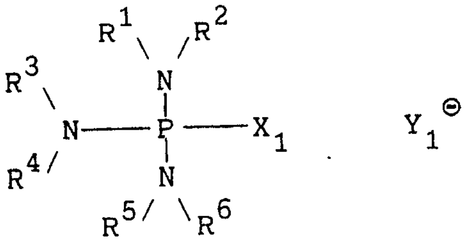
Formula H-VI



$$R^1-\underset{\displaystyle X^1}{\underset{|}{C}}=N-R^2$$

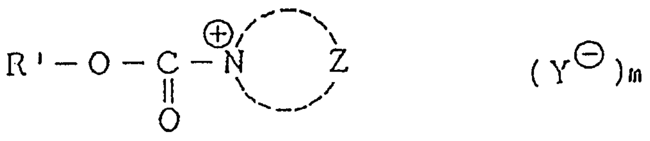
In the formula, R^1 and R^2 represents an alkyl group, an alkenyl group, a cycloalkyl group, an aryl group, an aromatic heterocyclic group or $-NR^3R^4$, where R^3 and R^4 represents an alkyl group, an alkenyl group, a cycloalkyl group, an aryl group or an aromatic heterocyclic group, including a group in which R^3 and R^4 have combined to form a ring. X_1 has the same definition as that for X_1 in Formula V.

Formula H-VII



In the formula, R^1 and R^2, R^3 and R^4, and R^5 and R^6, each have the same definitions as those for R^1 and R^2 in formula H-I. X_1 has the same definition as that for X_1 in Formula H-V, and $Y_1^{\ominus}$, for $Y_1^{\ominus}$ in Formula H-V.

Formula H-VIII



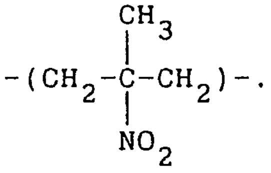
In the formula, R^1 represents an aryl group, Z represents a group of non-metallic atoms necessary to complete an aromatic heterocyclic ring, and a ring formed by R^1 and Z includes a ring having a substituent. $Y^\ominus$ represents an anion, and m represents 0 or 1. When an intramolecular salt is formed, m represents 0.

A carboxyl group reactive hardening agent preferably used in the present invention includes, for example, a methanesulfonic acid ester type hardening agent represented bv the following Formula H-IX, and what is called an ethyleneimine type hardening agent having two or more ethylenimino groups in its molecule, represented by the following Formula H-X. These methanesulfonic acid ester type hardening agent and ethyleneimine type hardening agent can be synthesized by a conventional method.

Formula H-IX

$CH_3SO_2O\text{-}R\text{-}OSO_2CH_3$

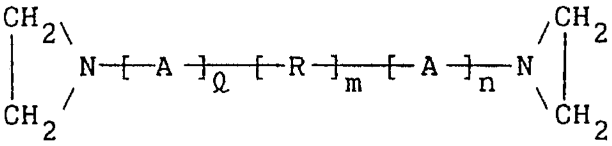
In the formula, R represents $-(CH_2)_2$, $-(CH_2)_3-$, $-(CH_2)4-$, $-(C_2H_4\text{-}O\text{-}C_2H_4)-$, $-(CH_2\equiv CCH_2)-$, or



$$-(CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle NO_2}{C}}-CH_2)-.$$

In particular, it is preferred that R is $-(CH_2)_3-$.

Formula H-X



In the formula, A represents $-SO_2-$, $-SO_2NH-$, -CO-, -COO-, -CONH-, -CSNH-, or $-PON(CH_2)_2NH-$. R represents an alkylene group, an arylene group, $-SiR_1R_2-$, $-PR_3R_4$, $-P(NC_2H_4)_2-$, or a nitrogen-containing heterocyclic group. These groups may have a substituent. R_1 and R_2 each represent an alkoxy group, R_3 represents a hydrogen atom, an alkoxy group, or a substituent such as $-N(CH_2)_2-$. The linkage A-R-A- may form a ring. ℓ, m and n each represent an integer.

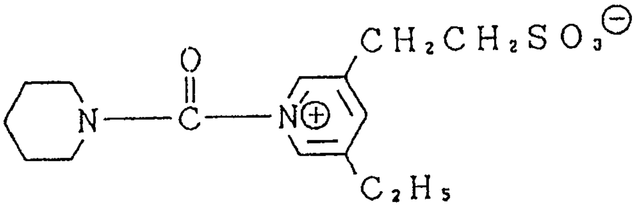
In addition to the compounds represented by the above Formulas H-I to H-X, the compounds as disclosed in Japanese Patent Publications Open to Public Inspection (hereinafter referred to as Japanese Patent O.P.I. publication) No. 38540/1975, No. 93470/1977, No. 43353/1981 and No. 113929/1983 and U.S. Patent No. 3,321,313 are also preferred as the carboxyl group reactive hardening agent used in the present invention.

Specific examples of the compound used in the present invention are sorted into groups as shown below. The compound of the present invention, however, is by no means limited to these.

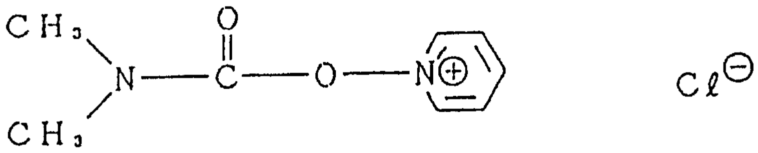
Exemplary compounds of the compound represented by Formula H-I:

(These compounds and synthesis methods therefor are detailed in Japanese Patent O.P.I. Publications No. 51945/1974, No 59625/1976, No. 9641/1986, No. 262854/1987 and No. 264044/1987.)

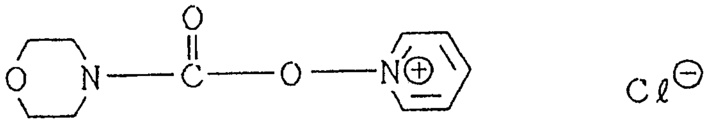
H－I－1



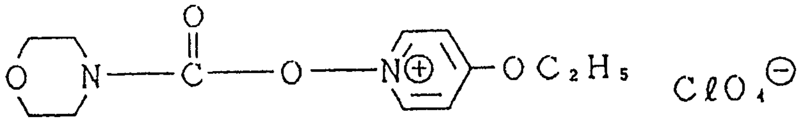
H－I－2



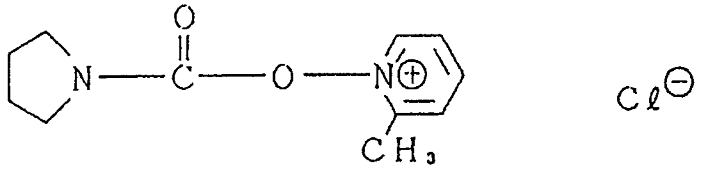
H－I－3



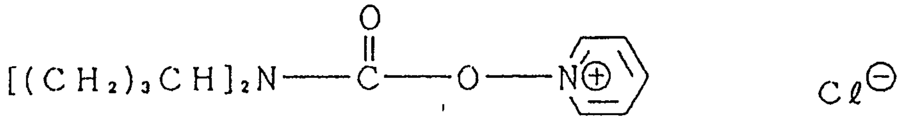
H－I－4



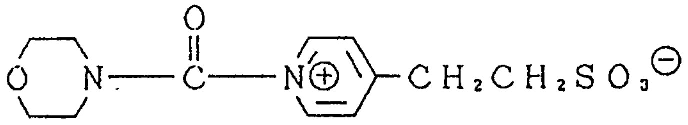
H－I－5



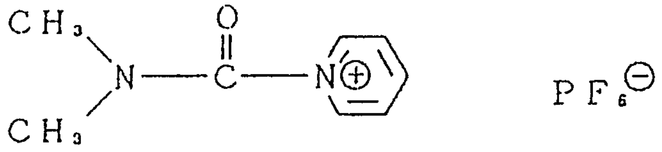
H－I－6



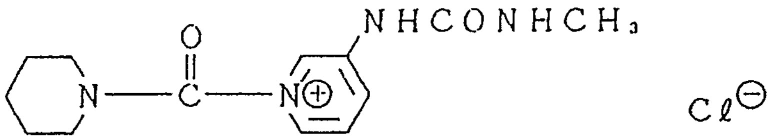
H－I－7



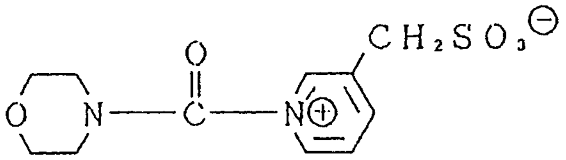
H－I－8



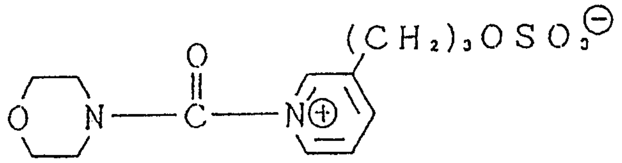
H－I－9



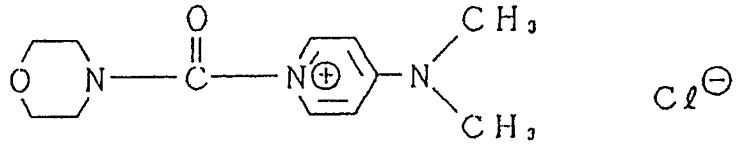
H－I－10



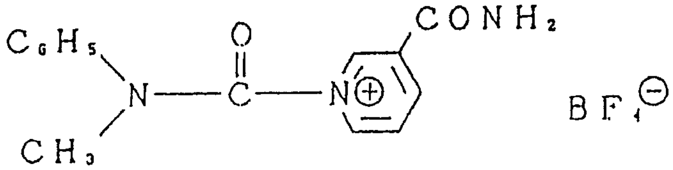
H－Ⅰ－11



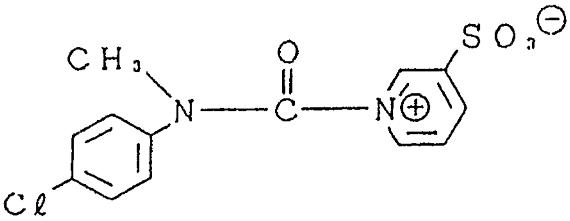
H－Ⅰ－12



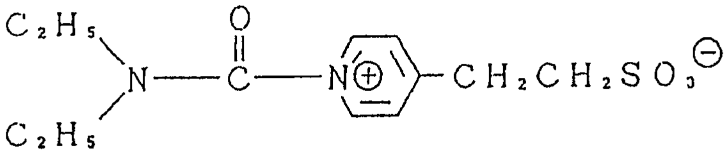
H－Ⅰ－13



H－Ⅰ－14

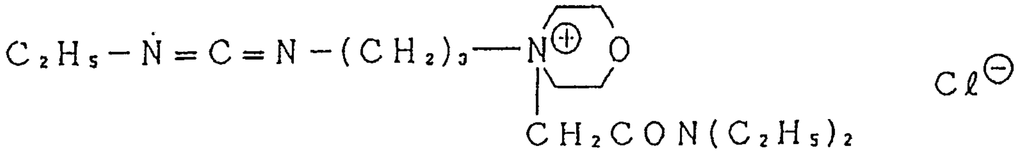


H－Ⅰ－15

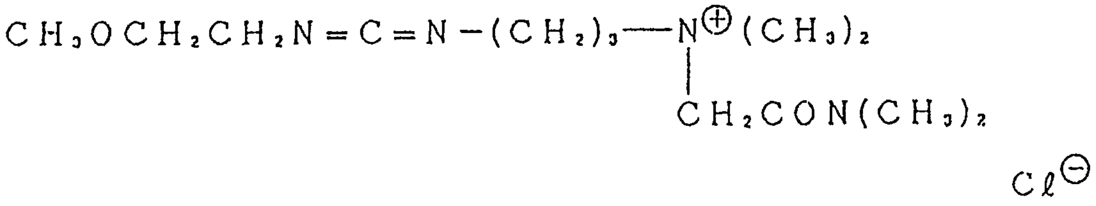


Exemplary compounds of the compound represented by Formula H-II:
These compounds and synthesis methods therefor are detailed in Japanese Patent O.P.I. Publications No 126125/1976 and No. 48311/1977.)

H－Ⅱ－1

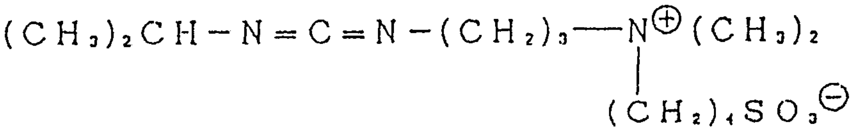


H－Ⅱ－2



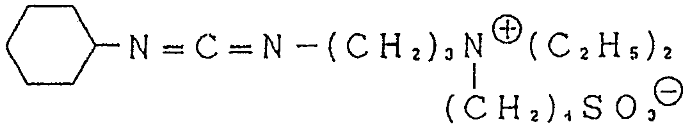
$$CH_3OCH_2CH_2N=C=N-(CH_2)_3-\underset{CH_2CON(CH_3)_2}{\underset{|}{N^{\oplus}}}(CH_3)_2 \qquad Cl^{\ominus}$$

H－Ⅱ－3

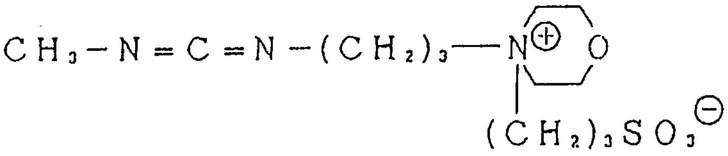


$$(CH_3)_2CH-N=C=N-(CH_2)_3-\underset{(CH_2)_4SO_3^{\ominus}}{\underset{|}{N^{\oplus}}}(CH_3)_2$$

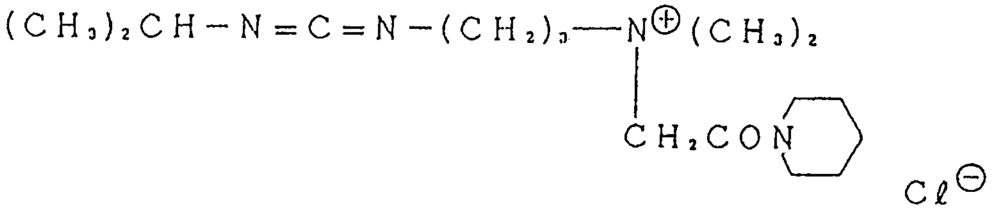
H－Ⅱ－4



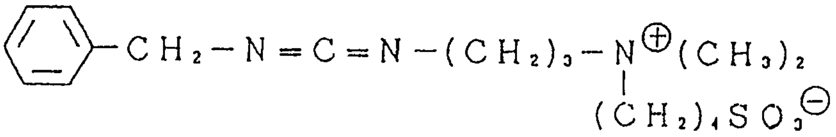
H－II－5



H－II－6



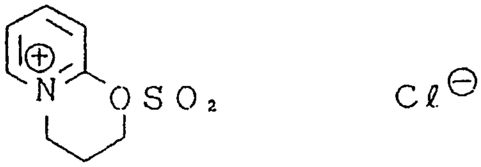
H－II－7



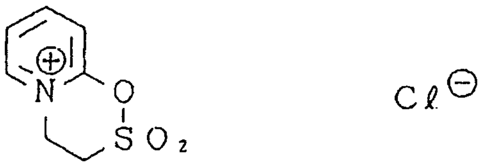
Exemplary compounds of the compound represented by Formula H-III:
(These compounds and synthesis methods therefor are detailed in Japanese Patent O.P.I. Publication No. 44140/1982, and Japanese Patent Examined Publications No. 46538/1982 and No. 50669/1983.)

H − Ⅲ − 1

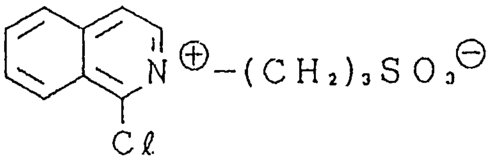
H − Ⅲ − 2



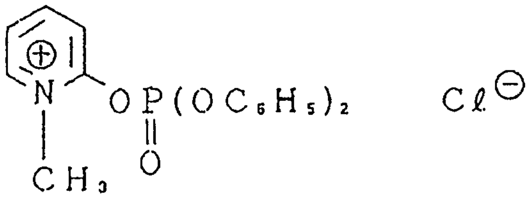
H − Ⅲ − 3



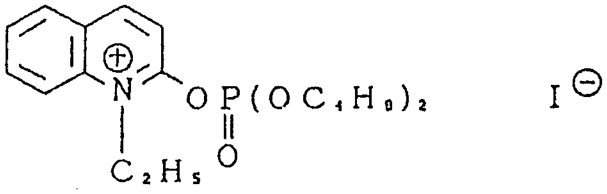
H − Ⅲ − 4



H − Ⅲ − 5

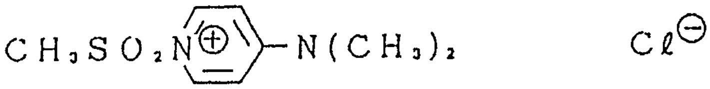


H − Ⅲ − 6

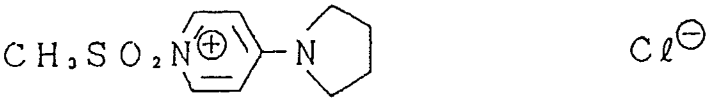


Exemplary compounds of the compound represented by Formula H-IV:
(These compounds and synthesis methods therefor are detailed in Japanese Patent O.P.I. Publication No. 54427/1977.)

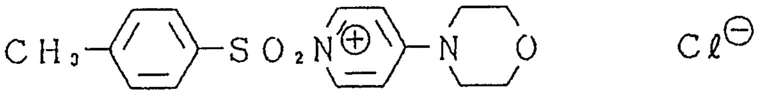
H－Ⅳ－1



H－Ⅳ－2



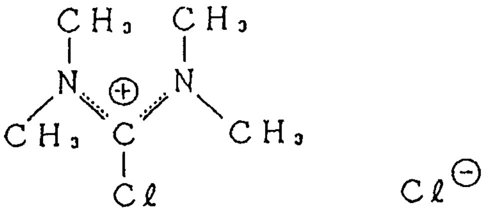
H－Ⅳ－3



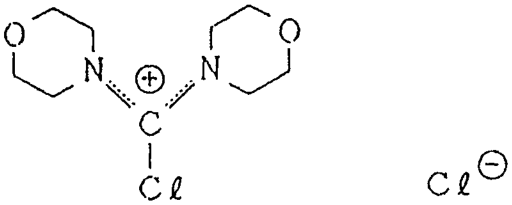
Exemplary compounds of the compound represented by Formula H-V:

(These compounds and synthesis methods therefor are detailed in Japanese Patent 0.P.I. Publications No. 225148/1985 and No. 240236/1986.)

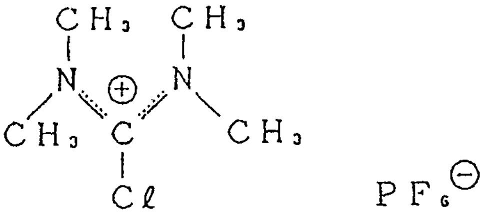
H－Ⅴ－1



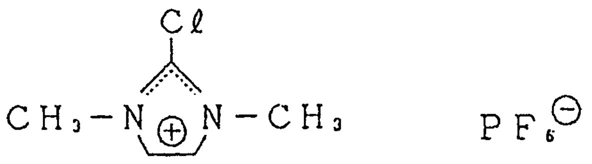
H－Ⅴ－2



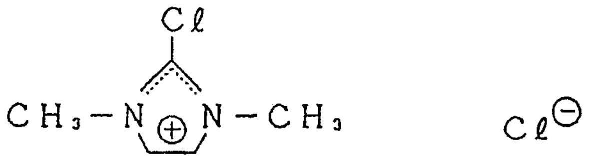
H－Ⅴ－3



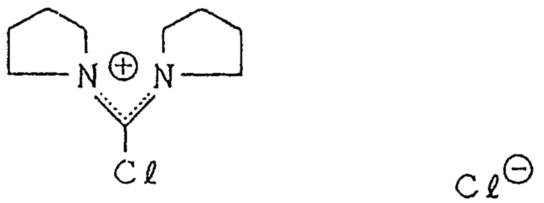
H－V－4



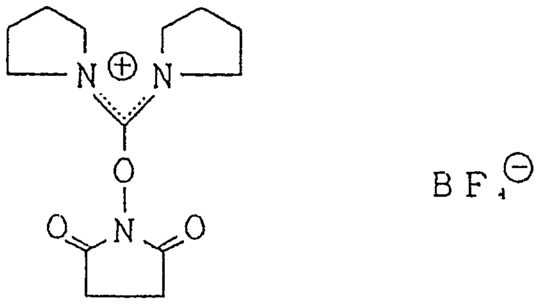
H－V－5



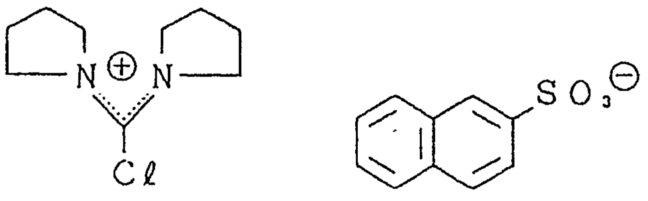
H－V－6



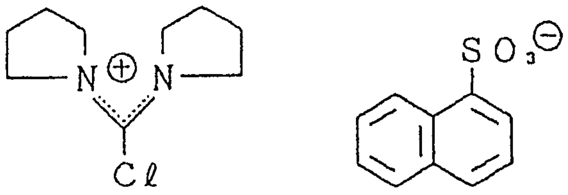
H－V－7



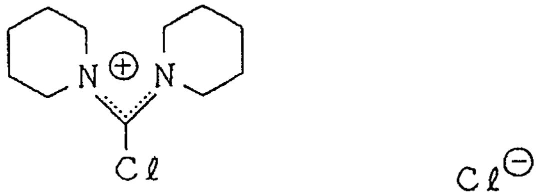
H－V－8



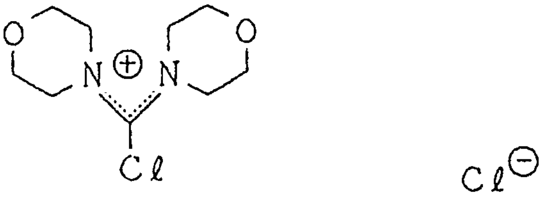
H-V-9



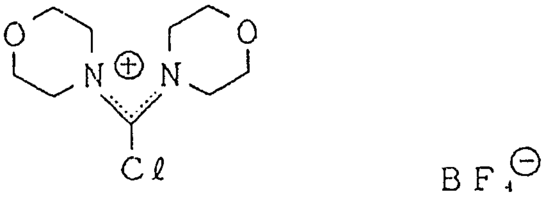
H-V-10



H-V-11

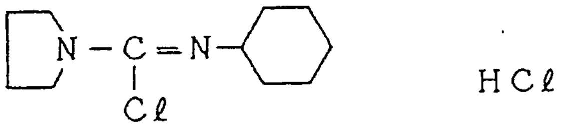


H-V-12

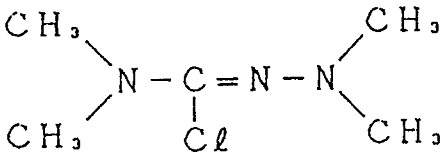


Exemplary compounds of the compound represented by Formula H-VI:
(These compounds and synthesis methods therefor are detailed in Japanese Patent O.P.I. Publications No 68866/1987 and No. 68867/1987.)

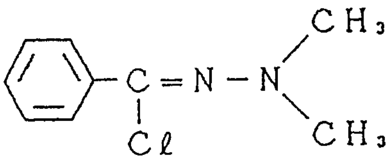
H - VI - 1



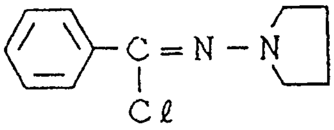
H - VI - 2



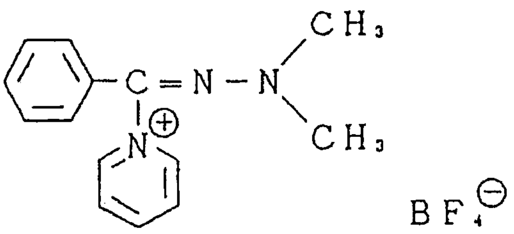
H - VI - 3



H - VI - 4



H - VI - 5



Exemplary compounds of the compound represented by Formula H-VII:
(These compounds and synthesis methods therefor are detailed in Japanese Patent O.P.I. Publication No. 128241/1986.)

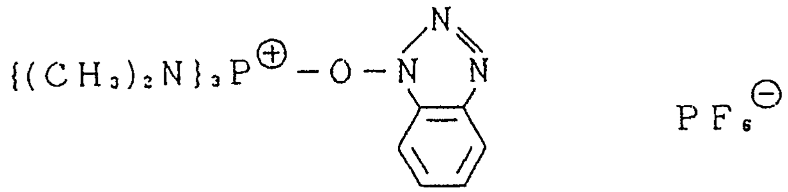
H－Ⅶ－1

$\{(CH_3)_2N\}_3P^{\oplus}-Cl \quad Cl^{\ominus}$

H－Ⅶ－2

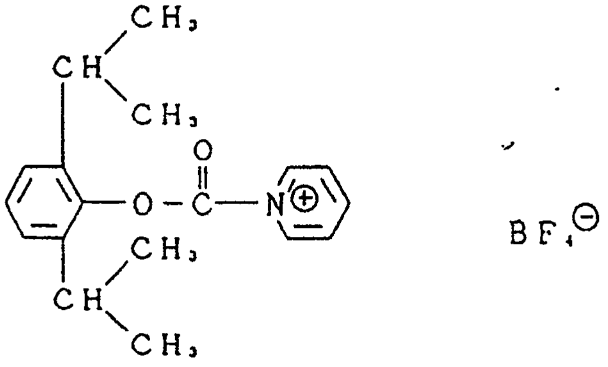
$\{(CH_3)_2N\}_3P^{\oplus}-Cl \quad BF_4^{\ominus}$

H－Ⅶ－3

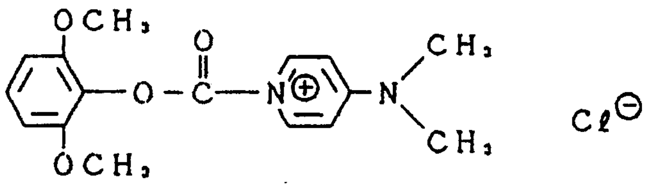


Exemplary compounds of the compound represented by formula H-VII:
(These compounds and synthesis methods therefor are detailed in Japanese Patent O.P.I. publication No. 234152/1987.)

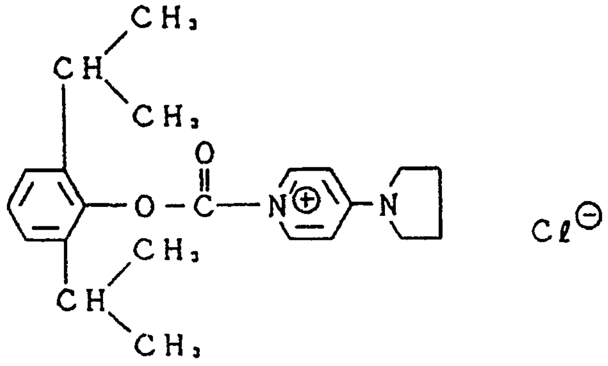
H − Ⅶ − 1



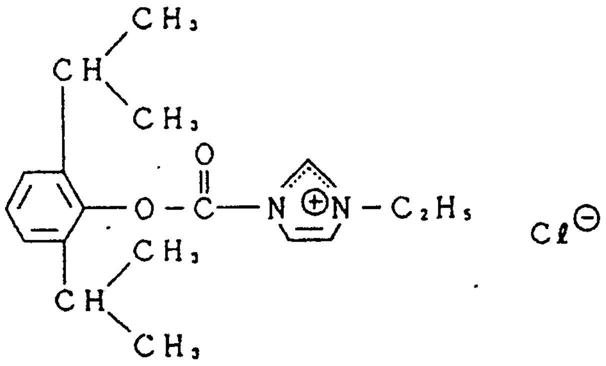
H − Ⅶ − 2



H − Ⅶ − 3



H − Ⅶ − 4



Exemplary compounds of the compound represented by Formula H-IX:

H－IX－1

$$CH_3SO_2O-(CH_2)_2-OSO_2CH_3$$

H－IX－2

$$CH_3SO_2O-(CH_2)_3-OSO_2CH_3$$

H－IX－3

$$CH_3SO_2O-(CH_2)_4-OSO_2CH_3$$

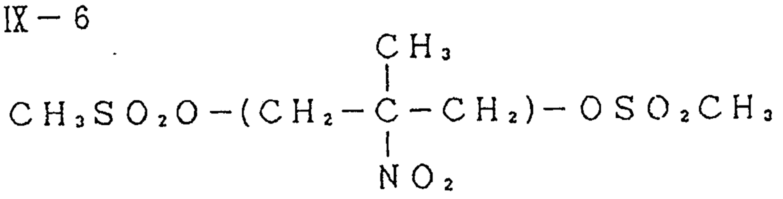
H－IX－4

$$CH_3SO_2O-(C_2H_4-O-C_2H_4)-OSO_2CH_3$$

H－IX－5

$$CH_3SO_2O-(CH_2C\equiv CCH_2)-OSO_2CH_3$$

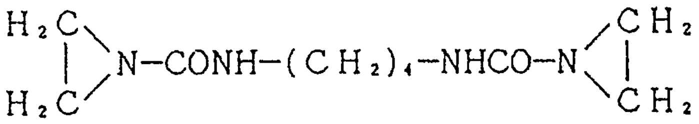
H－IX－6



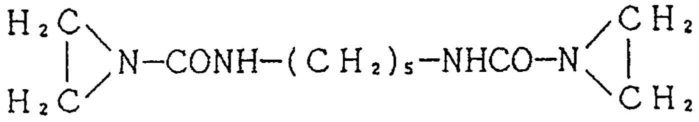
$$CH_3SO_2O-(CH_2-\underset{NO_2}{\overset{CH_3}{C}}-CH_2)-OSO_2CH_3$$

Exemplary compounds of the compound represented by Formula H-X:

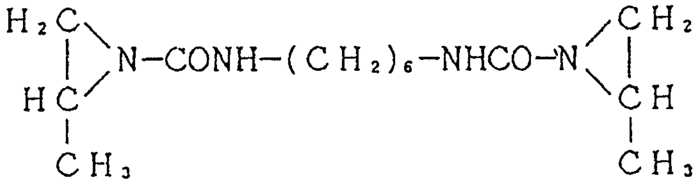
H－X－1



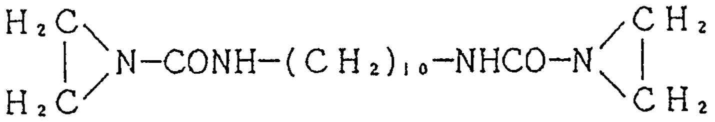
H－X－2



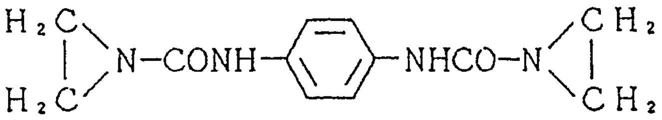
H－X－3



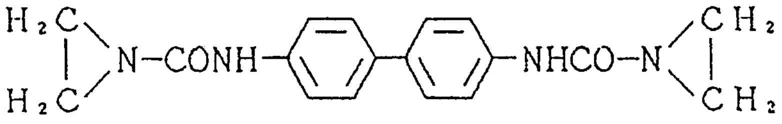
H－X－4



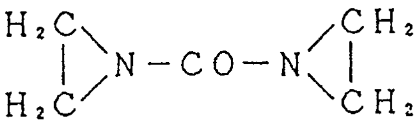
H－X－5



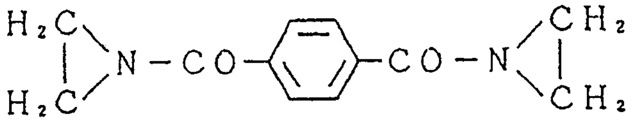
H－X－6



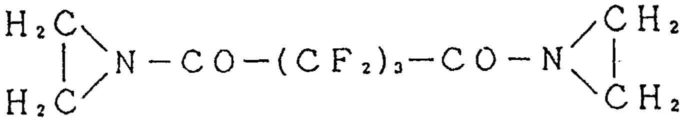
H－X－7



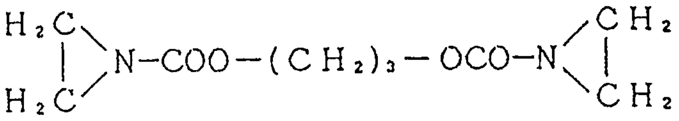
H－X－8



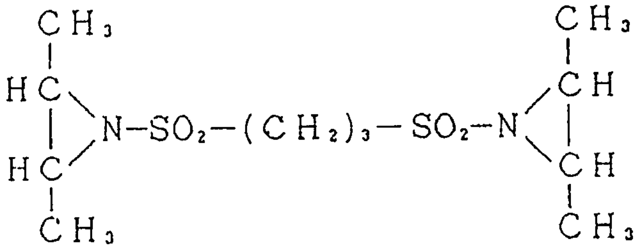
H－X－9



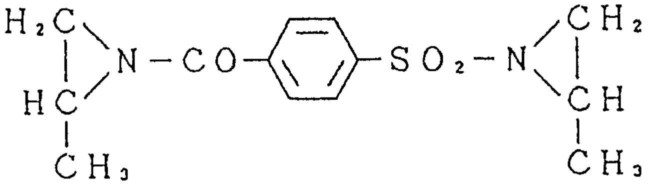
H－X－10



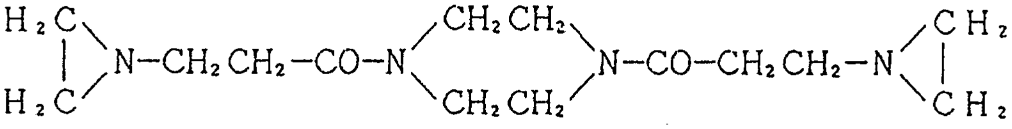
H－X－11



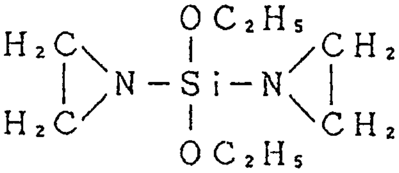
H－X－12



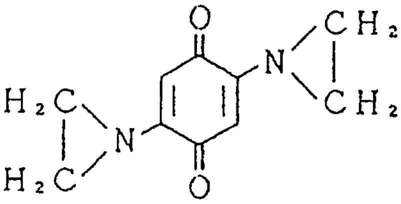
H−X−13



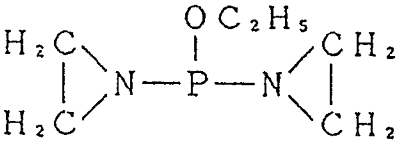
H−X−14



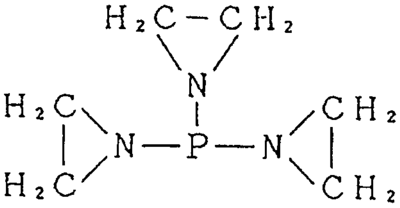
H−X−15



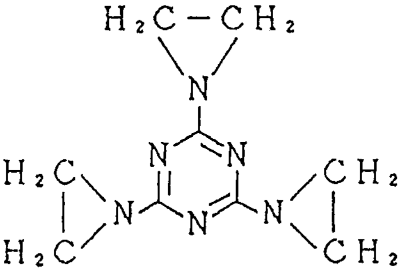
H−X−16



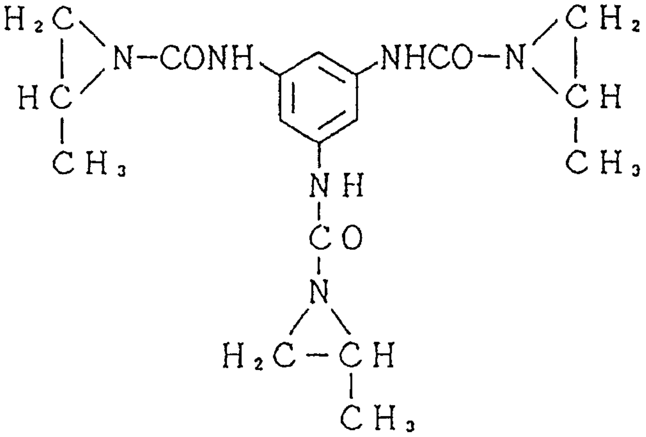
H−X−17



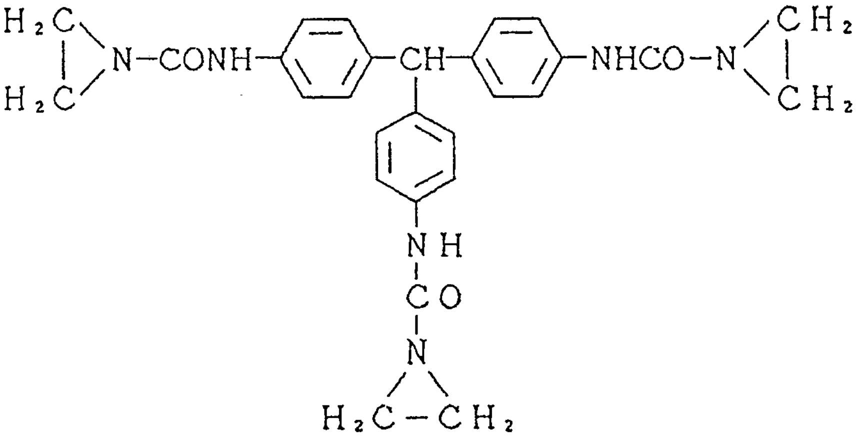
H−X−18



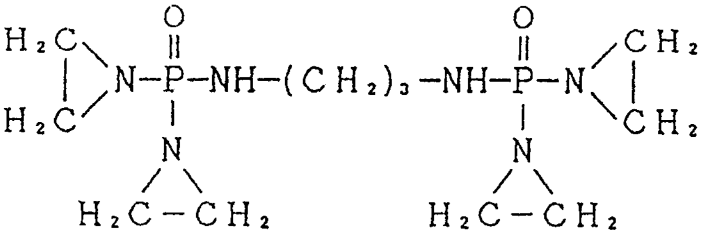
H−X−19



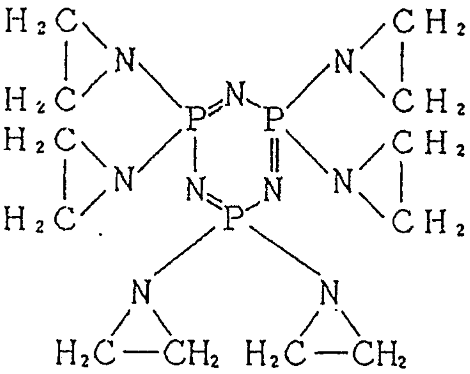
H−X−20



H-X-21

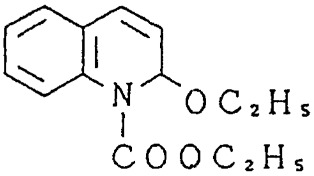


H-X-22

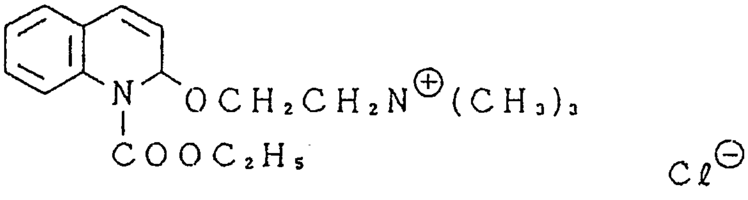


Compounds disclosed in Japanese Patent O.P.I. Publication No. 38540/1975:

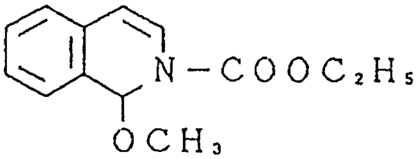
H-O-1



H-O-2

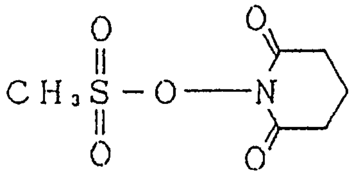


H-O-3

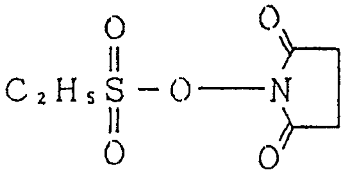


Compounds disclosed in Japanese Patent O.P.I. Publication No. 93470/1977:

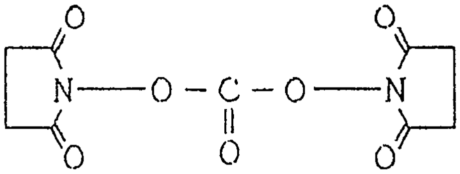
H - O - 4



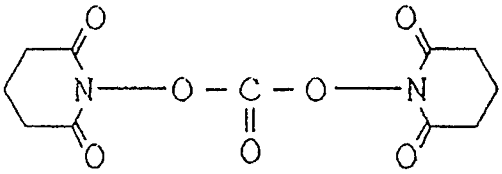
H - O - 5



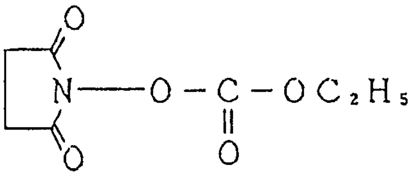
H - O - 6



H - O - 7

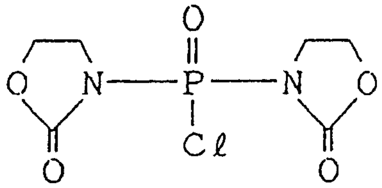


H - O - 8

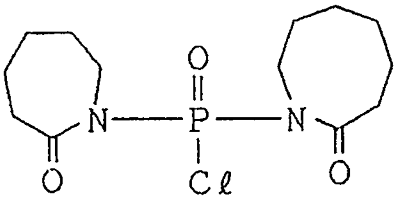


Compounds disclosed in Japanese Patent O.P.I Publication No. 113929/1983:

H－O－9

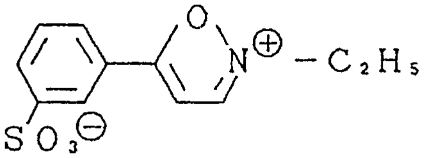


H－O－10

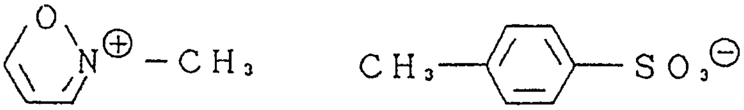


Compounds disclosed in U S. Patent No. 3,321,313:

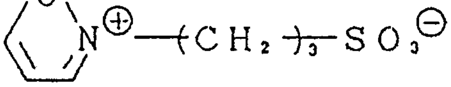
H－O－11



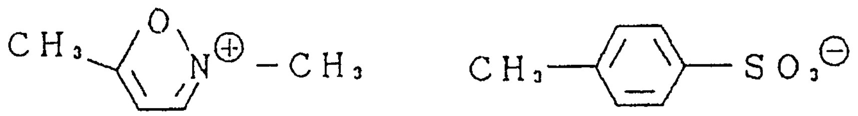
H－O－12



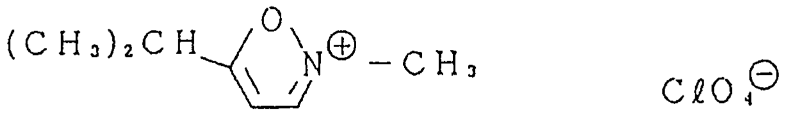
H－O－13



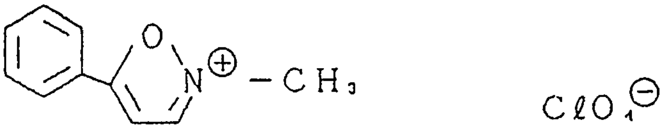
H-O-14



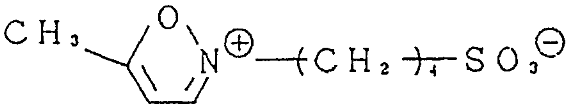
H-O-15



H-O-16



H-O-17



The carboxyl group reactive hardening agent used in the present invention may be in any amount selected depending on the purpose, but may preferably be used in an amount ranging from 3 x 10^{-5} to 15 x 10^{-5} mol per gram of a binder. Here, the binder refers to gelatin and the water-soluble polymeric compound previously described.

The carboxyl group reactive hardening agent and a hardening agent of a different type can be used in any proportion. The hardening agent of a different type may preferably be in the range of from 0.01 to 1 in weight ratio when the weight of the carboxyl group reactive hardening agent is assumed as 1.

The gelatin used in the subbing layer in the present invention includes lime-treated gelatin, acid-treated gelatin, and enzyme-treated gelatin as disclosed in Bull Soc. Sci. Phot. Japan, No. 16, p 30 (1966) as well as gelatin derivatives obtained by allowing a compound of various types such as an acid halide, an anhydride, isocyanates, bromoacetic acid, alkane sultones, vinyl sulfonamides, maleimide compounds, polyalkylene oxides and epoxy compounds to react with gelatin.

The subbing layer in the present invention may preferably be provided in a coating weight ranging from 0.05 g/m^2 to 1 g/m^2, and particularly from 0.1 g/m^2 to 0.5 g/m^2, in order to obtain a sufficient antistatic effect and achieve a good adhesion and a good sharpness of an image.

Various additives may also be optionally added to the subbing layer. For example, a matting agent such as amorphous silica may be added. The matting agent may preferably be added in an amount ranging from 1 % to 20 %, and particularly from 2 % to 12 %, in weight ratio based on a binder.

The substrate having a polyolefin resin surface in the present invention will be described below in detail.

The polyolefin resin includes homopolymers or copolymers of ethylene, propylene, butene, isoprene, pentene, methylpentene or the like. It is by no means limited to these.

The substrate on which the polyolefin resin is provided includes materials commonly used as supports, such as polyester and polypropylene. Polypropylene is preferred.

In the present invention, the polyolefin resin may be in the state of being exposed at the surface. Thus, the substrate includes not only a substrate covered with a polyolefin resin, but also a substrate which itself is formed of a polyolefin to have no coat layer, as exemplified by a substrate comprised of a single layer.

The substrate having a polyolefin resin surface in the present invention is exemplified by what is called a synthetic paper prepared by adding a filler and additives to polypropylene, mixing them to form a mixture, melt-kneading the mixture in an extruder, and then extruding the kneaded product from a die slit into a filmy sheet; what is called a laminated paper comprised of a wood-free paper, made from chemical pulp, coated with polyethylene; and a composite film comprised of a polyester coated with polyethylene containing titanium oxide,

In the present invention, the substrate having a polyolefin resin surface may preferably be provided on at least one surface thereof with a polyethylene layer.

The substrate of the present invention is preferably a film formed by biaxial orientation or stretching of a polypropylene resin containing an organic filler, and more preferably, a substrate having a polyethylene layer provided on said film.

The substrate having a polyolefin resin surface, used in the present invention, may preferably have a thickness of from 50 to 250 μm.

The substrate having a polyolefin resin surface, thus prepared, is coated on at least one surface thereof with a subbing layer coating solution containing at least the gelatin, the specific water-soluble polymeric compound represented by the general formula as previously described and the carboxyl group reactive hardening agent, and can be coated by various conventional methods. For example, it can be coated by roll coating, gravure coating, spray coating, air-knife coating, bar coating, dip coating, or curtain coating, which can be used alone or in combination.

The photographic paper support of the present invention, thus formed, is provided thereon with at least one light-sensitive silver halide photographic emulsion layer. Here, the support may optionally be applied with a surface-activating treatment such as corona discharge treatment before the light-sensitive silver halide photographic emulsion layer is provided.

A hydrophilic colloid that can be used in the present invention includes, for example, proteins such as gelatin, albumin, and casein; cellulose derivatives such as hydroxyethyl cellulose, carboxymethyl cellulose, and cellulose sulfate; sugar derivatives such as sodium alginate and starch derivatives; and various synthetic hydrophilic polymeric materials such as homopolymers or copolymers of polyvinyl alcohol, polyvinyl alcohol partial acetal, poly-N-vinylpyrrolidone, polyacrylic acid, polymethacrylic acid, polyacrylamide, polyvinylimidazole, polyvinylpyrazole, etc. Gelatin should preferably be used. Lime-treated gelatin, as well as acid-treated gelatin or enzyme-treated gelatin as disclosed in Bull. Soc. Sci. Phot. Japan, No. 16, p.30 (1966) may also be used as the gelatin. It is also possible to use a hydrolysate or enzymolysate of gelatin. The hydrophilic colloid may further include gelatin derivatives, and graft polymers of gelatin with other macromolecules.

In the present invention, any of usual various silver halide emulsions can be used as the silver halide emulsion used in at least one silver halide emulsion laver provided above the subbing layer. They include, for example, black and white photographic paper emulsions, black and white direct positive emulsions, usual color photographic paper negative emulsions, internal latent image type color photographic paper direct positive emulsions, and reversal emulsions.

In the case when an internal latent image type light-sensitive silver halide photographic material is used, the light-sensitive photographic material is provided with a silver halide emulsion layer containing an internal latent image type silver halide. As an emulsion for forming such an emulsion layer, it is possible to use conventionally known various internal latent image type silver halide emulsions. They include, for example, conversion silver halide emulsions as disclosed in U.S. Patent No. 2,592,250, laminated structure silver halide emulsions as disclosed in Japanese Patent Examined Publication No. 1412/1983, core/shell silver halide emulsions the inside of a particle of which has been chemically sensitized, as disclosed in Japanese Patent Examined Publications No. 34213/1977 and No. 55821/1985, and core/shell emulsions as disclosed in Japanese Patent Examined Publication No. 55820/1985.

These emulsions can be chemically sensitized by a conventional method, and also spectrally sensitized to any desired wavelength region by the use of a sensitizing dye.

An antifoggant, a stabilizer, a hardening agent, etc. can also be added to the silver halide emulsion. As a binder for the emulsion, the hydrophilic colloids as previously described can be used. It is advantageous to use gelatin.

Coating strength of silver halide emulsion layers and other hydrophilic colloid layers can be increased using a hardening agent. Such a hardening agent includes hardening agents of an aldehyde type, an aziridine type, an isoxazole type, an epoxy type, a vinylsulfone type, an acryloyl type, a carbodiimide type, a triazine type, and a polymer type, as well as a maleimide type, an acetylene type and a methane sulfonic acid ester type, which can be used alone or in combination These layers may also contain a plasticizer, a water-insoluble or sparingly soluble synthetic polymer dispersion (latex), a coupler, a coating aid, an antistatic agent, a formalin scavenger, a fluorescent brightening agent, a matting agent, a lubricant, an image stabilizer, a surface active agent, an anti-color-foggant, a development accelerator, a development restrainer, a bleach accelerator, etc.

As a coating method for light-sensitive photographic emulsion layers, extrusion coating or curtain coating is particularly useful since two or more layers can be simultaneously formed. The coating can be carried out at any desired speed, which, however, may preferably be at a speed of not less than 50 m/min in view of productivity.

EXAMPLES

The present invention will be described below in greater detail by giving Examples. In the following, "part(s)" refers to part(s) by weight.

Example 1

Preparation of Supports 1 to 5 :

A mixture comprising 80 parts of polypropylene with a melt index (MI) if 1 g/10 min., 19.9 parts of calcium carbonate of 1.5 µm in average particle diameter and 0.1 part of 2,6-di-tert-butyl-para-cresol (hereinafter "BHT") was melt-kneaded in an extruder and extruded therefrom into a sheet, followed by cooling. The resulting sheet was heated to 140° C, and then stretched by 4 times in the longitudinal direction to give a film. (Layer A)

Next, a mixture of 68.9 parts of polypropylene with an MI of 10 g/10 min., 0.1 part of BHT, 15 parts of talc fine powder of 2.0 µm in average particle diameter, 15 parts of rutile type titanium dioxide of 0.3 µ in particle diameter and 1.0 part of a fatty acid metal salt was melt-kneaded in an extruder, and extruded therefrom into a film. Immediately thereafter, the resulting film was laminated on both sides of the above film Layer A, followed by cooling while the films were nipped with rolls. A three-layer structure sheet was thus obtained. This three-layer structure film sheet was heated to 160° C, and then stretched bv about 10 times in the lateral direction to give a film with a thickness of 110 µ. Each layer of the resulting film had a thickness of 60 µm in respect of Layer A, and 25 µ for each of Layers B on its both sides. This was designated as Support 1.

One side of Support 1 was subjected to corona discharge treatment. and thereafter, using a melt extruder, coated with a resin composition comprising 30 parts of a master batch obtained by incorporating 80 % by weight of titanium oxide into a low-density polyethylene (density: 0.918; MI: 8.5), and 70 parts of the low-density polyethylene to have the coated resin layer thickness of 5 µ. This was designated as Support 2.

Next, a paper with a weight of 75 g/m^2 was made to travel at a speed of 80 m per minute, and the back side thereof was subjected to corona discharge treatment in a first zone. Thereafter, using a melt extruder, a resin composition comprising 50 parts of a low-density polyethylene (density: 0 918; MI: 5) and a high-density polyethylene (density: 0.965; MI: 7) was applied to the treated paper by melt extrusion coating in a coating weight of 16 g/m^2. A resin layer with a dull surface was thus formed. The surface of the paper was subjected to corona discharge treatment in a second zone. Thereafter, using a melt extruder, a resin composition comprising 80 parts of a master batch obtained by incorporating 80 % by weight of titanium oxide into a low-density polyethylene (density: 0 918; MI: 8.5), 45 parts of a low-density polyethylene (density: 0.918; MI: 5.0) and 25 parts of a high-density polyethylene (density: 0.965: MI: 7.0) was applied to the treated paper by melt extrusion coating in a coating weight of 16 g/m^2, thereby forming a resin layer with a semigloss surface. A polyethylene-coated paper with a thickness of 110 µ was thus obtained. This was designated as Support 3.

Using a same-directional rotation biaxial screw extruder (ZCM53/60, manufactured by Automatic Co.), 20 parts by weight of anatase-type titanium dioxide of 0.35 µ in average particle diameter and 80 parts by weight of polyethylene terephthalate with a specific viscosity of 0.80 were melt-kneaded, and thereafter the kneaded products was formed into pellets.

The resulting pellets were dried in vacuum at 180 °C for 6 hours. Then the dried pellets were melted in an extruder and thereafter extruded from a slit die onto a quench rotating drum to form an amorphous sheet with a sheet thickness of 420 µ. The sheet was then stretched by 2.6 times in the longitudinal direction at 95 °C and then stretched by 3.0 times in the lateral direction at 110 °C, which was subsequently thermally set at 210 °C, followed by cooling to give a white opaque film support with a thickness of 75 µm. This was designated as Support 4 (for comparison).

Next, one side of a transparent polyethylene terephthalate film with a thickness of 75 µ was subjected to corona discharge treatment, and thereafter, using a melt extruder, coated with a resin composition comprising 30 parts of a master batch obtained by incorporating 80 % by weight of titanium oxide into a low-density polyethylene (density: 0.918; MI: 8.5), and 70 parts of a low-density polyethylene to have a resin layer thickness of 30 µ. This was designated as Support 5.

Preparation of samples :

The surface of the resulting support was subjected to corona discharge treatment, and the support thus treated was provided with a subbing layer having the composition as shown in Table 1.

Subsequently, an internal latent image type color direct positive emulsion layer was formed according to the procedure described below.

Table 1

Subbing layer No.	Constituents of subbing layer (solid contents)				
	Gelatin	Water-soluble polymer		Hardening agent	
	Amount (pbw)		Amount (pbw)		Amount (pbw)
1 (X)	-	-	-	-	-
2 (X)	100	-	-	Triazine type *2, H-2	1
3 (X)	-	Exemplary compound (1)	100	Ethyleneimine type, M-X-3	1
4 (X)	-	Sodium polystyrene sulfonate (Chemistat, Sanyo Chemicals Co.)	100	-	-
5 (X)	1	Sodium polystyrene sulfonate (Chemistat, Sanyo Chemicals Co.)	99	-	-
6 (X)	65	Exemplary compound (1)	35	Triazine type *2, H-2	1
7 (X)	65	Exemplary compound (1)	35	Vinylsulfone type *1	2
8 (Y)	65	Exemplary compound (1)	35	Carboxyl group reactive hardening agent H-II-7	1
9 (Y)	65	Exemplary compound (1)	35	Carboxyl group reactive hardening agent H-IX-2 (Methane sulfonic acid ester type)	1
10 (Y)	65	Exemplary compound (1)	35	Carboxyl group reactive hardening agent H-X-3 (Ethyleneimine type)	1

X: Comparative Example, Y: Present Invention

*1: $CH_2=CH\text{-}SO_2CH_2OCH_2OCH_2SO_2CH=CH_2$

*2: The same as hardening agent H-2 used in the eighth layer described later.

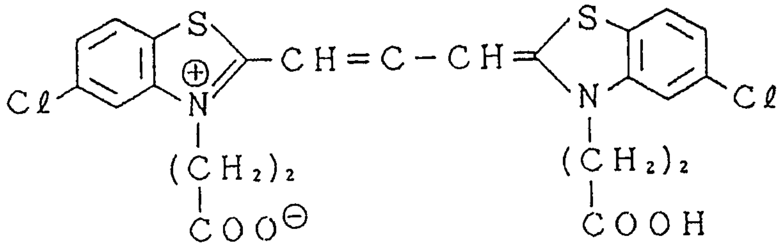
Red-sensitive emulsion layer: (First layer)

A 20 % inert gelatin solution was maintained at 50° C, into which the following Solution A and Solution B were simultaneously added and poured over a period of 3 minutes with stirring. After 10 minutes, Solution C was added over a period of 3 minutes. After ripening for 40 minutes, excess salts were removed by coagulation-washing. Thereafter, Solution D and Solution E were added so that silver chlorobromide comprising 95 mol % of AgCl and 5 mol % of AgBr was formed in layers on the surface. Excess water-soluble salts were again removed by coagulation-washing, followed by addition of gelatin in a small amount and then dispersion.

Solution A:	
Pure water	500 mℓ
NaCl	40 g (137 mol %)
KBr	8.9 g (15 mol %)
KI	0.4 g (0.5 mol %)
Solution B:	
Pure water	600 mℓ
$AgNO_3$	85 g
Solution C:	
Pure water	300 mℓ
KBr	50.6 (85 mol %)
Solution D:	
Pure water	1,500 mℓ
NaCl	20 g (114 mol %)
KBr	1.8 g (5 mol %)
Solution E:	
Pure water	500 mℓ
$AgNO_3$	51 g (0.3 mol %)

Thereafter, to the resulting silver halide emulsion, a solution containing the following sensitizing dye (I), 2,5-dioctylhydroquinone dispersed protectively with dibutylphthalate and the following cyan coupler (C-1), 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene, 1-phenyl-5-mercaptotetrazole, gelatin and the following coating aid (S-1) were added in appropriate amounts. Coating weight of silver was controlled to be 0.4 g/m^2.

(1)



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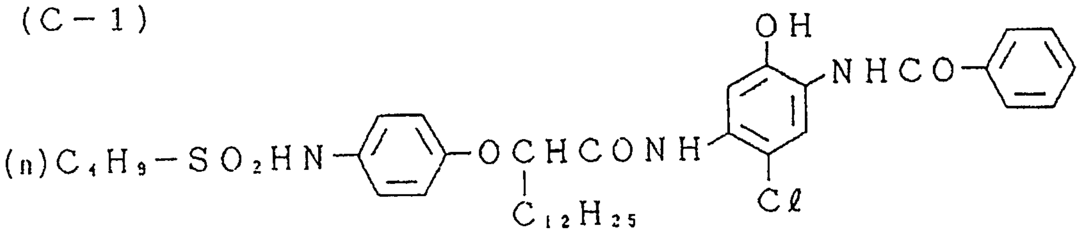

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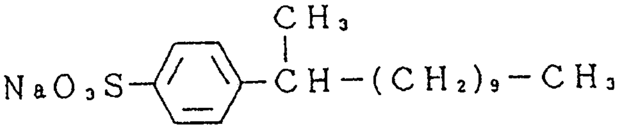


First intermediate layer: (Second layer)

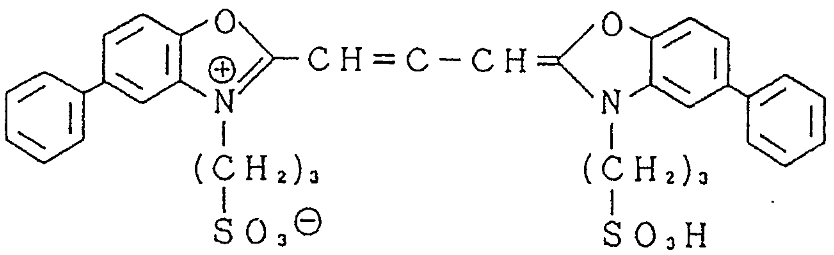
A gelatin solution containing 2,5-dioctyl hydroquinone and an ultraviolet absorbent Tinuvin 328 (a product of Ciba-Geigy Corp.), dispersed in dioctyl phthalate, and a coating aid (S-1) was prepared, and coated in a coating weight of Tinuvin 328, of 0.15 g/m^2.

Green-sensitive emulsion layer: (Third layer)

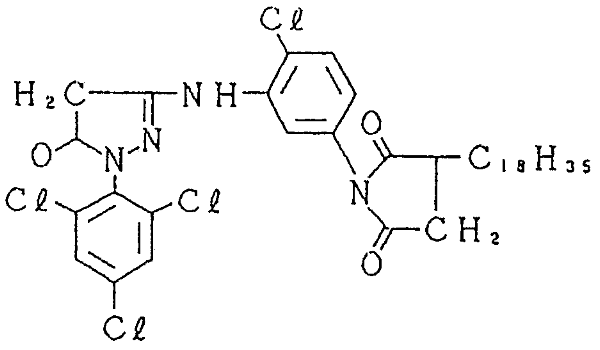
Silver halide grains were prepared in the same manner as for the red-sensitive emulsion. To the resulting emulsion, a solution containing the following sensitizing dye (II), 2,5-dioctylhydroquinone dispersed protectively with dibutyl phthalate and the following magenta coupler (M-1), 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene, 1-phenyl-5-mercaptotetrazole, gelatin and the following coating aid (S-2) were added in appropriate amounts.

Coating weight of silver was controlled to be 0.4 g/m^2.

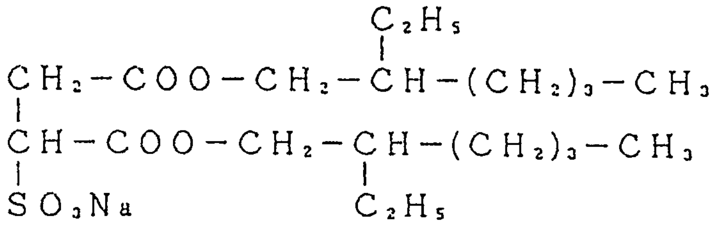
(II)



(M-1)



(S-2)



$$\begin{array}{l} C_2H_5 \\ | \\ CH_2-COO-CH_2-CH-(CH_2)_3-CH_3 \\ | \\ CH-COO-CH_2-CH-(CH_2)_3-CH_3 \\ | | \\ SO_3Na C_2H_5 \end{array}$$

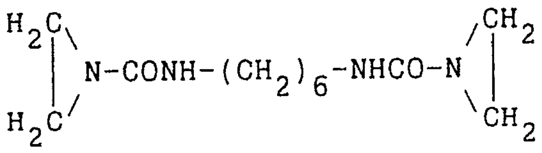
Second intermediate layer: (Fourth layer)

According to the same formulation as for the first intermediate layer. a gelatin solution was coated in a coating weight of Tinuvin 328, of 0.15 g/m^2.

Yellow filter layer: (Fifth layer)

Yellow colloidal silver prepared by oxidation in the presence of an alkaline weakly reducing agent (after neutralization, the weakly reducing agent was removed by noodle washing), a solution of 2,5-dioctyl hydroquinone dispersed in dioctyl phthalate, the above coating aid (S-1) and the following hardening agent (H-1) (added immediately before coating) were added. Coating weight of silver was controlled to be 0.1 g/m^2, and coating weight of gelatin, 0.9 g/m^2.

(H-1)



Third intermediate layer: (Sixth layer)

A gelatin solution containing the coating aid (S-1) was prepared, and coated in a coating weight of gelatin, of 0.5 g/m^2.

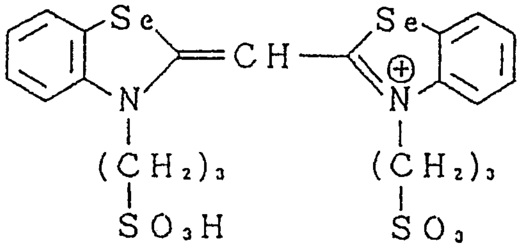
Blue-sensitive emulsion layer: (Seventh layer)

Here, the following emulsion was used: A 1.5 % inert gelatin solution was maintained at 60° C, into which the following Solution A and Solution B were simultaneously added and poured over a period of 15 minutes with stirring. After 15 minutes, Solution C was poured over a period of 2 minutes. After 1 minute, sodium thiosulfate was added in an amount corresponding to 3 mg/Ag, followed by ripening for further 40 minutes. The emulsion was sampled for analyzing its composition to reveal that it comprised silver chlorobromoiodide comprising 4 mol % of AgCl, 96 mol % of AgBr and 2 mol % of AgI. Excess salts were removed from this emulsion by coagulation-washing. Thereafter, Solution D and Solution E were added so that a surface layer comprising 97 mol % of AgCl and 3 mol % of AgBr was formed in layers. Thereafter, excess water-soluble salts were again removed by coagulation-washing, followed by addition of gelatin for dispersion.

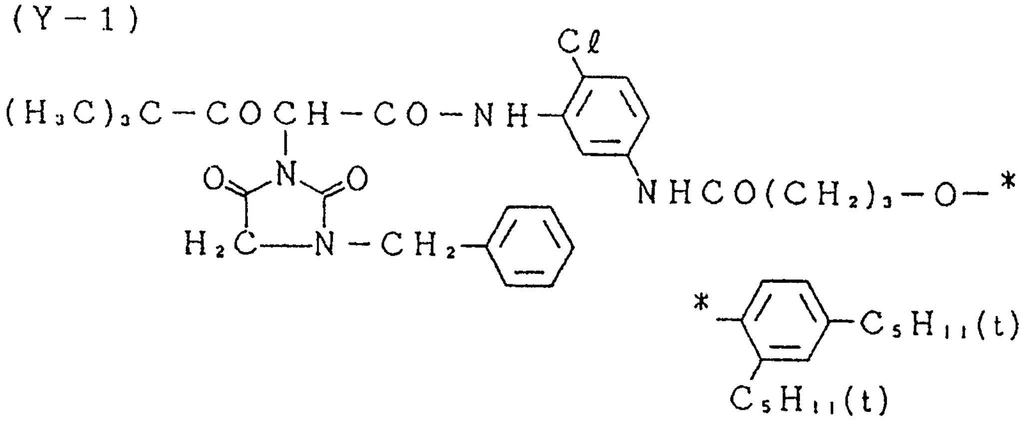
Solution A:	
Pure water	1,000 mℓ
NaCl	76 g
KBr	17 g
Hexachloroiridiate (III)	2×10^{-5} g
Solution B:	
Pure water	1,000 mℓ
$AgNO_3$	169.9 g
Solution C:	
Pure water	800 mℓ
KBr	103 g
KI	3.3 g
Solution D:	
Pure water	500 mℓ
$AgNO_3$	51 g
Solution E:	
Pure water	500 mℓ
NaCl	25.8 g
KBr	1.1 g

Next, a solution containing the following sensitizing dye (III) and the following yellow coupler (Y-1) dispersed in dioctyl phthalate, and 2-mercaptobenzothiazole, 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindene, gelatin, the following coating aid (S-3) and the following hardening agent (H-3) (added immediately before coating) were added. This solution was coated so as to give a coating weight of silver, of 0.5 g/m².

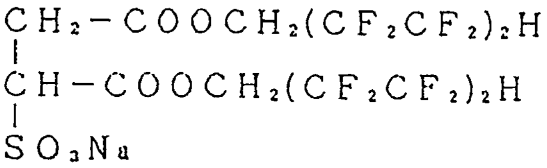
(III)



(Y－1)



(S－3)



$$\begin{array}{l} CH_2-COOCH_2(CF_2CF_2)_2H \\ | \\ CH-COOCH_2(CF_2CF_2)_2H \\ | \\ SO_3Na \end{array}$$

Fourth intermediate layer: (Eighth layer)

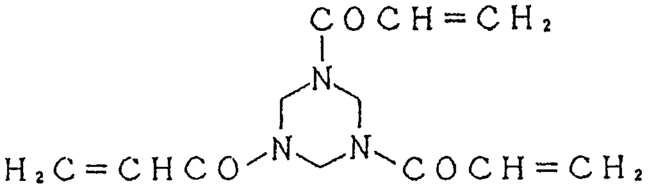
In the same manner as for the first intermediate layer, a gelatin solution was coated in a coating weight of Tinuvin 328, of 0.15 g/m². Here, a hardening agent (H-3) was added immediately before coating.

Protective layer: (Ninth layer)

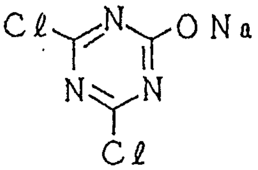
A gelatin solution containing colloidal silica, a coating aid (S-3) and hardening agents (H-2) and (H-3) (added immediately before coating) were coated in a coating weight of gelatin, of 1.0 g/m²

On a surface-treated polyethylene laminate paper, the 9 layers of from the red-sensitive emulsion layer to the protective layer were provided by simultaneous coating and then dried.

(H-2)



(H-3)



These samples were each incubated so that the emulsion layers were hardened to an appropriate degree, and thereafter, a cross-cut adhesion test, a static mark test, a handling test and a daylight exposure test were carried out. These tests were carried out in the following way.

- Cross-cut adhesion test -

A sample was immersed for 2 minutes in a developing solution kept at 38° C. Thereafter, an emulsion layer was scratched with claws made of iron, in a lattice pattern. The layer was rubbed with fingers to observe whether it was peeled. A state in which the lattice pattern completely remained was evaluated as "A"; a state in which the layer remained beyond that, as "AA"; a state in which corners of the lattice were rounded, as "B"; and a state in which the layer was completely peeled, as "C".

- Static mark test -

Each sample was cut in a length of 89 mm x 1 m, and the cut was looped up around three rolls made of rubber, in a darkroom kept at a relative humidity of 30 %. The looped sample was rolled in the state that the sample and the rolls did not slip. Thereafter, the sample was processed to examine whether or not static marks occurred because of peel charging. A state in which no fog occurred was evaluated as "A"; a state in which static marks slightly occurred in dots on the edge, as "B"; a state in which static marks occurred in lines on the edge, as "C"; and a state in which static marks occurred areally, as "D".

- Daylight exposure test after processing -

Samples having been subjected to wedge expcsure were exposed to sunlight for 60 days to carry out a daylight exposure test.

An instance in which an image layer was peeled from a support at the edge was evaluated as "C"; and an instance in which no peeling occurred, as "A".

Results of the above are shown in Tables 2 to 4.

Table 2

(Cross-cut adhesion test results)					
	Support No.				
Subbing layer No.	Support 1 (Y)	Support 2 (Y)	Support 3 (Y)	Support 4 (X)	Support 5 (Y)
1 (X)	C	C	C	C	C
2 (X)	C	C	C	C	C
3 (X)	C	C	C	C	C
4 (X)	C	C	C	C	C
5 (X)	C	C	C	C	C
6 (X)	C	C	C	C	C
7 (X)	C	C	C	C	C
8 (Y)	B	A	A	C	A
9 (Y)	A	AA	A	C	A
10 (Y)	A	AA	A	C	A
X: Comparative Example, Y: Present Invention					

Table 3

(Static mark test results)					
	Support No.				
Subbing layer No.	Support 1 (Y)	Support 2 (Y)	Support 3 (Y)	Support 4 (X)	Support 5 (Y)
1 (X)	C	C	B	D	D
2 (X)	C	C	B	D	D
3 (X)	A	A	A	B	B
4 (X)	A	A	A	B	B
5 (X)	A	A	A	B	B
6 (X)	A	A	A	B	B
7 (X)	A	A	A	B	B
8 (Y)	A	A	A	B	B
9 (Y)	A	A	A	B	B
10 (Y)	A	A	A	B	B
X: Comparative Example, Y: Present Invention					

As will be evident from Tables 2 and 3, the samples of the present invention show satisfactory results in both the cross-cut adhesion test and the static mark test at the same time.

Table 4

(Daylight exposure test after processing)					
	Support No.				
Subbing layer No.	Support 1 (Y)	Support 2 (Y)	Support 3 (Y)	Support 4 (X)	Support 5 (Y)
8 (Y)	C	A	A	C	A
9 (Y)	C	A	A	C	A
10 (Y)	C	A	A	C	A
X: Comparative Example, Y: Present Invention					

As will be evident from Table 4, Supports 2, 3 and 5 provided with the polyethylene layer are seen to have superior light resistance.

Next, using 5 kinds of samples in which the subbing layer No. 9 was provided and supports were replaced with those of Nos. 1 to 5, copy sheets for maps of an A0 size were prepared, and a handling test was carried out. Comparisons were made on whether a sheet was liable to crease and had a tear strength.

Table 5

(Handling test results)	
Support	
No. 1:	Hard to crease, and greatly tear-resistant
No. 2:	Hard to crease, and greatly tear-resistant
No. 3:	Easy to crease, and little tear-resistant
No. 4:	Easy to crease, but greatly tear-resistant
No. 5:	Easy to crease, but greatly tear-resistant

It is seen from the results that the polypropylene synthetic paper has a great resistance to creasing and tear, is tough against various handling, and thus is suited for large-sized prints such as maps.

As will be evident from the above results, the substrate having a polyolefin surface and provided thereon with the subbing layer according to the present invention gives a light-sensitive photographic material having a good adhesion of emulsion to support. In particular, use of a methanesulfonic acid ester type hardening agent or ethyleneimine type hardening agent as the carboxyl group reactive hardening agent for the subbing layer is seen to bring about a further superior adhesion of emulsion to support.

Of the substrate having a polyolefin surface, what is called a synthetic paper, i.e., a substrate made of an opaque resin film prepared by using a polypropylene resin as a main material, adding an inorganic filler to the resin, and forming a film by biaxial stretching, has not only water resistance, smoothness and print adaptability but also flexibility, cutting strength, tensile strength, tear strength, etc. Thus, the substrate of this type is seen to be preferably used for large-sized photographs such as maps and posters, or photographic seals. In particular, when what is called the synthetic paper is provided on its surface with a thin polyethylene layers the image forming section may not be peeled even if exposed to daylight, thus having a superior light resistance.

Example 2

On the support 2 as used in Example 1, a subbing layer was formed. Here, the ratio of the water-soluble polymeric compound (1) to gelatin in the subbing layer was varied as shown in Table 6, H-IX-2 was used as the carboxyl group reactive hardening agent, and the coating weight of solid content of the subbing layer was controlled to be 0.2 g/m^2. Subsequently, on the subbing layer thus formed, emulsion layers were formed in the same manner as in Example 1. Samples 1 to 9 were thus prepared.

These samples were each incubated so that the emulsion layers were hardened to an appropriate degree. Thereafter, a cross-cut adhesion test was carried out. Results obtained are shown in Table 6.

Table 6

(Ratios of water-soluble polymeric compound to gelatin, and cross-cut adhesion test results)

Sample No.	(A) Amount	(B) Amount	(A)/(B)	(C) Amount	Adhesion test results
	part(s)	parts		part	
1	-	99	0	1	C
2	1	98	0.01	1	C
3	5	94	0.05	1	B
4	9	90	0.1	1	A
5	33	66	0.5	1	AA
6	71	28	2.5	1	A
7	82.5	16.5	5.0	1	A
8	90	9	10.0	1	B
9	99	-	Infinity	1	C

(A): Water-soluble polymeric compound (1)
(B): Gelatin
(C): Hardening agent (H-IX-2)

As will be evident from Table 6, the ratio of water-soluble polymeric compound to gelatin is seen to be preferable when it is in the range of from 0.1 to 5.0.

Example 3

On the support 2 as used in Example 1, a subbing layer was formed. Here, the coating weight of solid content of the subbing layer was controlled to be 0.2 g/m^2, using the water-soluble polymeric compound (1) in an amount of 33 parts as solid content and 66 parts of gelatin, and varying the coating weight of the carboxyl group reactive hardening agent H-IX-2 as shown in Table 7. Incubation was carried out as shown in Table 7. Subsequently, emulsion layers were formed in the same manner as in Example 1. Samples 1 to 9 were thus prepared. These samples were each again incubated so that the emulsion layers were hardened to an appropriate degree. Thereafter, a cross-cut adhesion test was carried out. Results obtained are shown in Table 7.

Table 7

(Ratios of hardening agent to binder, and cross-cut adhesion deterioration with time of subbed products)

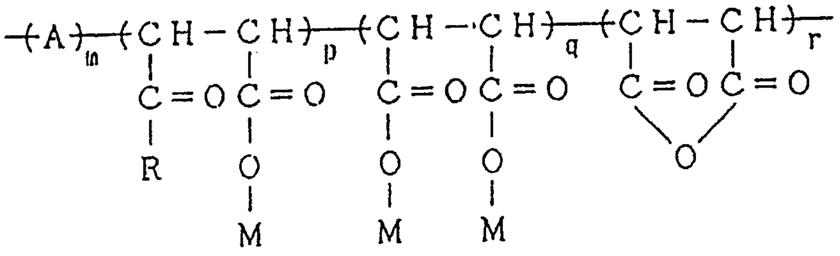
Sample No.	Coating weight of hardening agent H-IX-2 (mol/g•binder) x 10^{-5} mol	Cross-cut adhesion: No incubation after subbing	Cross-cut adhesion: Incubated at 40°C, 80 % RH for 3 days after subbing
1	0.5	C	C
2	1.0	B	B
3	2.0	B	A
4	3.0	A	A
5	5.0	A	A
6	10	A	A
7	15	A	A
8	20	A	C
9	25	A	C

As will be evident from Table 7, use of the hardening agent in an excessively small amount results in a poor adhesion, and use thereof in an excessively large amount tends to cause deterioration of adhesion with time when the incubation is carried out after subbing. Taking these into consideration together, the coating weight of the hardening agent is seen to be preferable when it is in the range of from 3 x 10^{-5} mol/g•binder to 15 x 10^{-5} mol/g•binder.

Claims

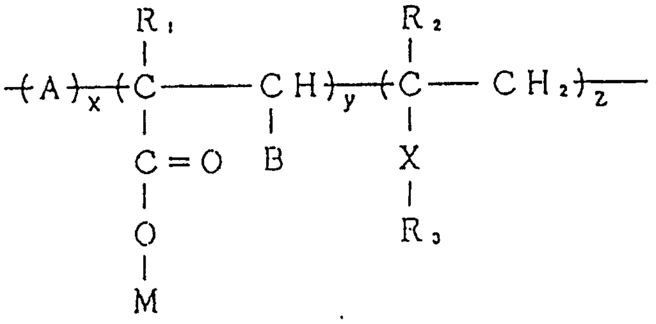
1. A support for a photographic paper comprising a substrate having a polyolefin resin on its surface, and, provided thereon, a subbing layer containing gelatin, a water-soluble polymeric compound represented by the following General formula and a carboxyl group reactive hardening agent;

General formula



$$-(A)_m-(\underset{\substack{|\\C=O\\|\\R}}{CH}-\underset{\substack{|\\C=O\\|\\O\\|\\M}}{CH})_p-(\underset{\substack{|\\C=O\\|\\O\\|\\M}}{CH}-\underset{\substack{|\\C=O\\|\\O\\|\\M}}{CH})_q-(\underset{\substack{|\\C=O}}{CH}-\underset{\substack{|\\C=O}}{CH})_r- \quad \text{(the two C=O of the last unit joined through O)}$$

or



$$-(A)_x-(\overset{\substack{R_1\\|}}{\underset{\substack{|\\C=O\\|\\O\\|\\M}}{C}}-\underset{\substack{|\\B}}{CH})_y-(\overset{\substack{R_2\\|}}{\underset{\substack{|\\X\\|\\R_3}}{C}}-CH_2)_z-$$

wherein A represents a vinyl monomer; B represents a hydrogen atom, -COOM or -COR, provided the B represents a hydrogen atom when Z is 0 or R_1 is an alkyl group; M represents a hydrogen atom or a cation, provided the cation is substituted at a rate of not less than 10 % based on all of M contained in said water-soluble polymeric compound; R represents $-OR'$ or $-NR'R''$ wherein R' represents an alkyl group, an aralkyl group, an aryl group, a heterocyclic residual group or a non-metallic atom necessary to complete a heterocyclic ring together with R'', and R'' represents a hydrogen atom, a lower alkyl group or a non-metallic atom necessary to complete a heterocyclic ring together with R'; R_1 and R_2 each represent a hydrogen atom or a lower alkyl group; X represents -COO- or -OC-O-; R_3 represents a halogenoalkyl group or a halogenoalkyloxyalkyl group; m, p, q, r, x, y and z each represent a value to show mol % of each monomer where m is 40 to 60, p is 0 to 60, q is 0 to 50, r is 0 to 5, X is 0 to 70, Y is 20 to 80, and z is 0 to 80, provided that $m + p + q + r = 100$ and $x + y + z = 100$.

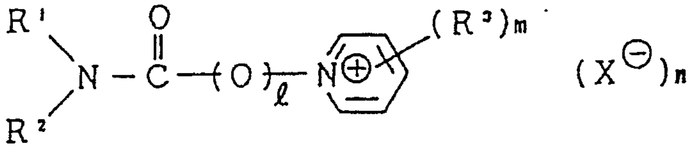
2. The support of claim 1, wherein the weight ratio of said water-soluble polymeric compound to said gelatin ranges from 0.1 to 5.0.

3. The support of claim 1, wherein said water-soluble polymeric compound is contained in an amount of from 10 to 800 mg/m².

4. The support of claim 1, wherein said water-soluble polymeric compound is contained in an amount of from 30 to 400 mg/m².

5. The support of claim 1, wherein said carboxyl group reactive hardening agent is selected from the group consisting of compounds represented by following formulae, H-I , H-II , H-III , H-IV, H-V, H-VI, H-VII, H- VIII, H-IX , and H-X;

formula H- I



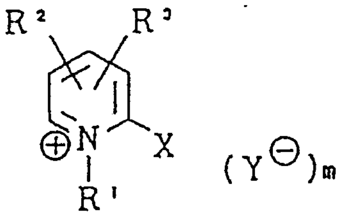
wherein R^1 and R^2 each represent an alkyl group or an aryl group or combine to form a heterocyclic ring together with a nitrogen atom; R^3 represents a substituent; m represents 0 to 5, provided that when $m \geq 2$, a plural number of R^3 are the same as or different from each other; $X^{\ominus}$ represents an anion; ℓ represents 0 or 1; n represents 0 to 2, provided that n is 0 when an intramolecular salt is formed;

formula H-II

$R^1 - N = C = N - R^2$

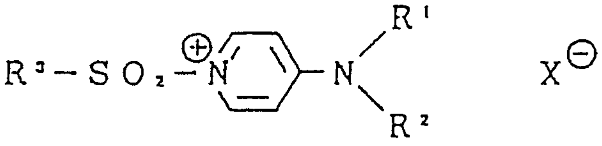
wherein R^1 and R^2 each represent an alkyl group, a cycloalkyl group, an aralkyl group, an alkoxyalkyl group or a group represented by $-R^3\text{-}N\ R^4R^5R^{6\oplus}X^{\ominus}$ wherein R^3 represents an alkylene group, R^4, R^5 and R^6 each represent an alkyl group or two of R^4 to R^6 may combine to form a heterocyclic ring together with a nitrogen atom, $X^{\ominus}$ represents an anion;

formula H-III



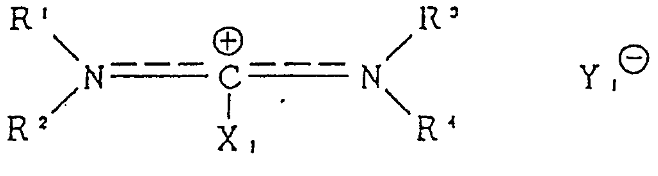
wherein R^1 represents an alkyl group, an aralkyl group or an aryl group; R^2 and R^3 each represent a hydrogen atom or substituent or combine to form a heterocyclic ring together with a pyridinium ring skelton; X represents a group capable of being split off upon reaction with a nucleophilic reagent; $Y^{\ominus}$ represents an anion; m represents 0 or 1, provided that m is 0 when an intramolecular salt is formed;

formula H-IV



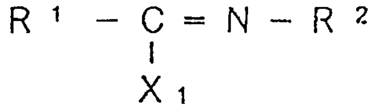
wherein R^1 and R^2 represent the same as in H-I; R^3 represents an alkyl group, aralkyl group or an aryl group; X$^\ominus$ represents an anion;

formula H-V



wherein R^1 and R^2, and R^3 and R^4 each represent the same as R^1 and R^2 in H-I or R^1 and R^3 may combine to form a ring; X$_1$ represents a group capable of being split off upon reaction with a nucleophilic reagent; Y$_1$$^\ominus$ represents an anion;

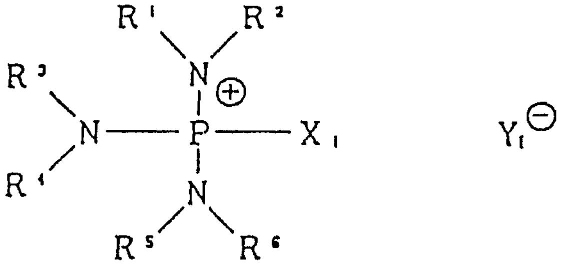
formula H-VI



$$R^1-\underset{\substack{|\\X_1}}{C}=N-R^2$$

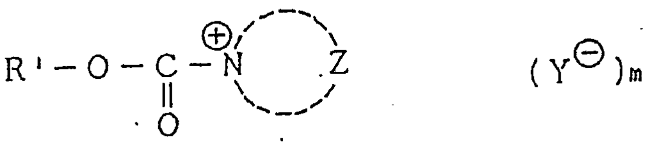
wherein R^1 and R^2 represent an alkyl group, an alkenyl group, a cycloalkyl group, an aryl group, an aromatic heterocyclic group or -NR^{3}R^4 where R^3 and R^4 represent an alkyl group, an alkenyl group, a cycloalkyl group, an aryl group or an aromatic heterocyclic group or combine to form a ring; X$_1$ represent a group capable of being split off upon reaction with a nucleophilic reagent;

formula H-VII



wherein R^1 and R^2, R^3 and R^4, and R^5 and R^8 each represent the same as R^1 and R^2 in H-I; X$_1$ represents a group capable of being split off upon reaction with a nucleophilic reagent; Y$_1$$^\ominus$ represent an anion;

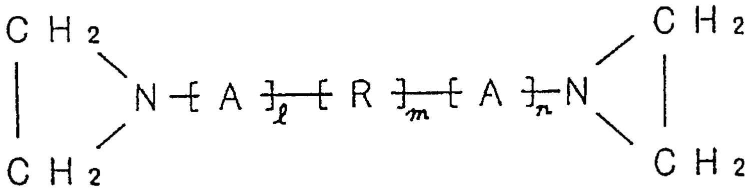
formula H-VIII



wherein R^1 represent an aryl group; Z represent a group of non-metallic atoms necessary to form an aromatic heterocyclic ring; Y$^\ominus$ represent an anion; m is 0 or 1, provided that m is 0 when an intramolecular

salt is formed;
formula H-IX
CH_3SO_2O-R-OSO_2CH_3
wherein R represents -$(CH_2)_2$-, -$(CH_2)_3$-, -$(CH_2)_4$-, - (CH_2H_4-O-C_2H_4)-, ($CH_2C{\equiv}CCH_2$)- or -{$CH_2C(CH_3)(NO_2)CH_2$}-;

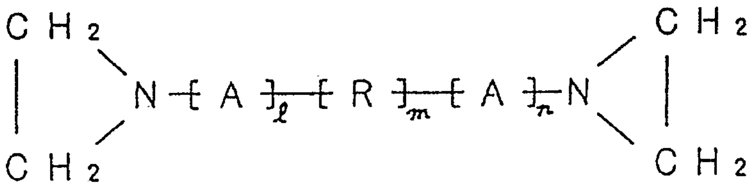
formula H-X



wherein A represents -SO_2-, -SO_2NH-, -CO-, -COO-, -CONH-, -CSNH- or -PON$(CH_2)_2$NH-; R represents an alkylene group, an arylene group, -SiR_1R_2-, -PR_3R_4-, -P$(NC_2H_4)_2$- or a nitrogen-containing heterocyclic group wherein R_1 and R_2 each represent an alkoxy group, R_3 represents a hydrogen atom, an alkoxy group or -N$(CH_2)_2$-, -A-R-A- may form a ring; ℓ, m and n each represent an integer.

6. The support of claim 1, wherein said carboxyl group reactive hardening agent is selected from the group consisting of compounds represented by following formulae, H-IX and H-X;
formula H-IX
CH_3SO_2O-R-OSO_2CH_3
wherein R represents -$(CH_2)_2$-, -$(CH_2)_3$-, -$(CH_2)_4$-, -(C_2H_4-O-C_2H_4)-, -($CH_2C{\equiv}CCH_2$)- or - {$CH_2C(CH_3)(NO_2)CH_2$}-;

formula H-X



wherein A represents -SO_2-, -SO_2NH-, -CO-, -COO-, -CONH-, -CSNH- or -PON$(CH_2)_2$NH-; R represents an alkylene group, an arylene group, -SiR_1R_2-, -PR_3R_4-, -P$(NC_2H_4)_2$- or a nitrogen-containing heterocyclic group wherein R_1 and R_2 each represent an alkoxy group, R_3 represents a hydrogen atom, an alkoxy group or -N$(CH_2)_2$,-, -A-R-A- may form a ring; ℓ, m and n each represent an integer.

7. The support of claim 1, wherein the content of said carboxyl group reactive hardening agent ranges from 3×10^{-5} to 15×10^{-5} mol per 1 g of said gelatin and said water-soluble polymeric compound.

8. The support of claim 1, wherein the coating weight of said subbing layer ranges from 0.05 to 1 g/m^2.

9. The support of claim 1, wherein the coating weight of said subbing layer ranges from 0.1 to 0.5 g/m^2.

10. The support of claim 1, wherein said substrate consists of polypropylene.

11. The support of claim 1, wherein said substrate has a film formed by biaxial orientation or stretching of a polypropylene resin containing an inorganic filler.

12. The support of claim 1 or 2, wherein a polyethylene layer is provided on the said substrate.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 90 11 5702

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	US-A-3062674 (R.C.HOUCK ET AL) * claim 1 * * column 11, lines 21 - 23 * *Example X* ---	1-12	G03C1/93 G03C1/89
Y	US-A-4268623 (H.SERA ET AL) * claim 1 * * column 12, lines 55 - 57 * * column 2, lines 39 - 42 * ---	1-12	
Y	US-A-4113918 (M.KOGURE ET AL) * abstract * ---	1-4	
Y	US-A-3888679 (H.KOMATSU) * abstract * * column 4, line 57 - column 7, line 30 * * column 5, line 8 * ---	5-7, 10-12	
Y	PATENT ABSTRACTS OF JAPAN vol. 11, no. 208 (P-593)(2655) 07 July 1987, & JP-A-62 030244 (KONISHIROKU PHOTO INDUSTRY CO LTD) 09 February 1987, * the whole document * -----	5-9	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

G03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	16 NOVEMBER 1990	BOLGER W.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
& : member of the same patent family, corresponding document