(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 227 840 A1**

(12) EUROPEAN PATENT APPLICATION

published in accordance with Art. 158(3) EPC

(21) Application number: **86904357.0**

(51) Int. Cl.⁴: **G 03 G 9/12**

(22) Date of filing: **30.06.86**

Data of the international application taken as a basis:

(86) International application number: **PCT/JP 86/00333**

(87) International publication number: **WO 87/00308 (15.01.87 87/1)**

(30) Priority: **01.07.85 JP 142565/85**

(43) Date of publication of application: **08.07.87 Bulletin 87/28**

(84) Designated Contracting States: **BE DE FR GB**

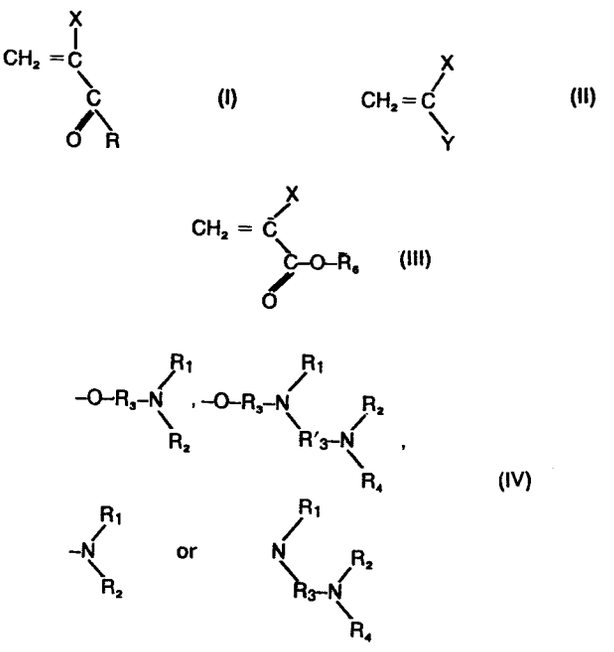
(71) Applicant: **TOA PAINT CO., LTD., 3-18, Takami 1-chome Konohana-ku, Osaka-shi Osaka 554 (JP)**

(72) Inventor: **TANGE, Toyokichi, 6-3-302, Sengen-cho, Hiratsuka-shi Kanagawa 254 (JP)**
Inventor: **MARUYAMA, Masatoshi, 13-6, Yuhigaoka, Hiratsuka-shi Kanagawa 254 (JP)**
Inventor: **NISHIZONO, Shoko, 136, Saitobun-cho Kanagawa-ku, Yokohama-shi Kanagawa 221 (JP)**
Inventor: **MINAGAWA, Tomohiko, 6-12-309, Sakae Satte-machi, Kitakatsushika-gun Saitama 340-01 (JP)**

(74) Representative: **Kraus, Walter, Dr. et al, Patentanwälte Kraus, Weisert & Partner Thomas-Wimmer-Ring 15, D-8000 München 22 (DE)**

(54) RESIN DISPERSION.

(57) A resin dispersion suited as electrophotographic liquid developer for offset master, which contains in a highly insulating hydrocarbon medium: (A) a copolymer substantially insoluble in said medium and containing (i) 20 to 99.5 wt % of vinyl acetate, (ii) 0.5 to 12 wt % of a monomer represented by formula (I), (wherein R represents formula (IV), R_1, R_2, and R_4 each independently represents hydrogen, C_{1-6} alkyl, or alkoxyalkyl containing 1 to 4 carbon atoms in each alkyl moiety, R_3 and R'_3 each independently represents C_{1-4} alkylene, and X represents hydrogen or methyl), and (iii) O to 79.5 wt % of C_{1-20} alkyl ester and/or C_{3-8} cycloalkyl ester of acrylic or methacrylic acid (provided that the sum of (i), (ii), and (iii) is 100 wt %), with at least part of said monomer (I) being quaternized in its amino group with a quaternizing agent; and (B) a copolymer substantially soluble in said medium and containing (iv) 95 to 15 wt % of a monomer of formula (II), (wherein X is as defined above, Y represents $-COOR_5$, $-OCOR_5$ or $-OR_5$, and R_5 represents C_{4-20} alkyl), (v) 5 to 85 wt % of a monomer of formula (III), (wherein X is as defined above, and R_6 represents C_{3-8} cycloalkyl or aralkyl containing 1 to 3 carbon atoms in the alkyl moiety) (provided that the sum of (iv) and (v) is 100 wt %), and (vi) 0 to 2 wt % (in terms of sulfur content) of an organic mercaptan having at least one thiol group (provided that the sulfur content is represented by weight in terms of a sulfur content based on the soluble copolymer).



EP 0 227 840 A1

SPECIFICATION

RESIN DISPERSION

Technological Field

This invention provides a novel resin dispersion useful as an electrophotographic liquid developer for offset masters, and particularly, to a novel resin dispersion capable of giving a liquid developer which has excellent dispersion stability and forms an image being free from blurring or backgrounding and having excellent printing resistance.

Background Technology

One resin dispersion for use in an electrophotographic liquid developer heretofore proposed is a resin dispersion obtained by graft-polymerizing a monomer capable of forming a polymer insoluble in an organic solvent having a low dielectric constant and high electrical insulation (to be referred to as "solvent" hereinafter) onto a polymer soluble in the solvent (for example Japanese Laid-Open Patent Publication No. 54029/1978). Such a resin dispersion is complex to produce, and also has the disadvantage that a developer prepared from it frequently undergoes gellation and is difficult to maintain stable.

Attempts have been made in recent years to remove the defects of such a graft copolymer resin dispersion. A technique has been disclosed by which the stability of a resin dispersion comprising a solvent-soluble polymer and a solvent-insoluble polymer is improved by introducing polar functional groups such as $-COOH$, $-SO_3H$ or $-OCOCH_3$ into both of these polymers and thus utilizing adsorptive power between the polar functional group of the soluble polymer and the polar functional group of the insoluble polymer (for example

Japanese Laid-Open Patent Publication No. 83174/1984).

It has been found that although the above resin dispersion comprising the soluble and insoluble polymers in both of which the polar functional groups are simply introduced is improved to some extent in stability, it frequently gives rise to blurring (blurring of contours) or backgrounding, and particularly when it is used as an electrophotographic liquid developer for an offset master, the printing resistance of the offset master is not always sufficient.

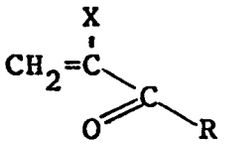
The present invention gives a solution to the above problems of the prior art, and provides a resin dispersion for use as an electrophotographic liquid developer having good stability, freedom from image blurring or backgrounding and very good printing resistance.

The backgrounding denotes a phenomenon in which in offset printing, the printing ink adheres to a non-image area to smudge it. Furthermore, in offset printing, as the number of printing cycles increases, the image area on the offset master is attacked by the solvent of the printing ink. As a result, a phenomenon occurs in which the printing ink fails to adhere to the image area. The printing resistance denotes a property in which this phenomenon does not occur.

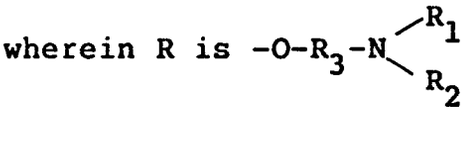
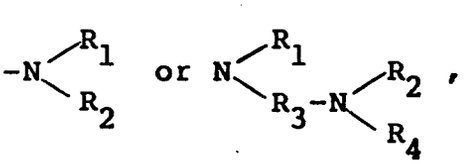
Disclosure of the Invention

According to this invention, there is provided a resin dispersion suitable as an electrophotographic liquid developer for offset masters, said dispersion comprising in a highly insulating hydrocarbon medium,

(A) a copolymer substantially insoluble in said medium and containing (i) 20 to 99.5% by weight, preferably 50 to 99.5% by weight, most preferably 70 to 99.5% by weight, of vinyl acetate, (ii) 0.5 to 12% by weight, preferably 2 to 12% by weight, most preferably 2 to 6% by weight, of a monomer of the formula



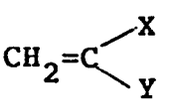
(I)

wherein R is  ,  ,

 or , in which R_1, R_2 and R_4, independently from each other, represent hydrogen, C_{1-6} alkyl, or alkoxyalkyl containing 1 to 4 carbon atoms in each alkyl moiety, R_3 and R'_3, independently from each other, represent C_{1-4} alkylene, and X represents hydrogen or methyl,

and (iii) 0 to 79.5% by weight, preferably 2 to 48% by weight, most preferably 5 to 28% by weight, of a C_{1-20} alkyl ester and/or a C_{3-8} cycloalkyl ester of acrylic or methacrylic acid (provided that the sum of (i), (ii) and (iii) is 100% by weight), with at least part of said monomer of formula (I) being quaternized in its amino group with a quaternizing agent to convert it into a quaternary ammonium compound, and

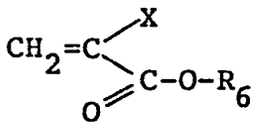
(B) a copolymer substantially soluble in said medium and containing (iv) 95 to 15% by weight, preferably 80 to 40% by weight, most preferably 75 to 65% by weight, of a monomer of the formula



(II)

wherein X is as defined above, Y represents $-COOR_5$, $-OCOR_5$ or $-OR_5$, and R_5 represents C_{4-20} alkyl,

(v) 5 to 85% by weight, preferably 20 to 60% by weight, most preferably 25 to 35% by weight, of a monomer of the formula



(III)

wherein X is as defined above, and R_6 represents C_{3-8} cycloalkyl or aralkyl containing 1 to 3 carbon atoms in the alkyl moiety,

(provided that the sum of (iv) and (v) is 100% by weight), and (vi) 0 to 2% by weight, preferably 0.03 to 2% by weight, most preferably 0.1 to 1% by weight, especially 0.2 to 0.3% by weight (in terms of sulfur content) of an organic mercaptan having at least one thiol group (provided that the sulfur content is the sulfur content of the soluble copolymer in % by weight).

The monomer of formula (I) in (ii) contained in the insoluble copolymer may include esters of acrylic or methacrylic acid with alcohols, for example, mono- or di-methylaminoethyl alcohol, mono- or di-ethylaminoethyl alcohol, mono- or di-methylaminopropyl alcohol, mono- or di-ethylaminopropyl alcohol, mono- or di-phenylaminomethyl alcohol, mono- or di-phenylethyl alcohol, dimethoxyaminoethyl alcohol, diethoxyaminoethyl alcohol, mono- or dimethylaminopropylaminoethyl alcohol, and mono- or diethylaminopropylaminoethyl alcohol. Of these monomers of formula (I), dialkylaminoalkyl esters of methacrylic acid are preferred, and dimethylaminoethyl methacrylate and diethylaminoethyl methacrylate are especially preferred.

Examples of the monomers of formula (I) in (ii) also include acid amides formed between acrylic or methacrylic acid with amines, for example mono- or di-methylamine, mono- or di-ethylamine, mono- or di-propylamine, mono- or di-methylaminoethylamine, mono- or di-ethylaminoethylamine, mono- or di-methylaminopropylamine and

mono- or di-ethylaminopropylamine. Among these monomers of formula (I), acid amides between acrylic or methacrylic acid and dialkylamines or dialkylaminoalkylamines, particularly dimethylamine, diethylamine or dimethylaminopropylamine, are preferred.

At least one monomer of formula (I) may be included in the insoluble copolymer. If the content of the monomer of formula (I) exceeds 12% by weight, the hydrophilicity of the image becomes high and the ink receptivity at the time of offset printing is reduced undesirably. If it is less than 0.5% by weight, the printing resistance is reduced undesirably.

At least part of the monomer of formula (I) contained in the insoluble copolymer (particularly the monomer contained on, or near, the surface of the dispersed particles) is quaternized in its amino group with a quaternizing agent to convert it into a quaternary ammonium compound. Preferably, in the insoluble copolymer, the amount of the quaternizing agent used is 0.1 to 5 mole%, more preferably 0.5 to 2 mole%, based on the monomer of formula (I). If the amount of the quaternizing agent exceeds 5 mole%, the image density is decreased. Furthermore, since the hydrophilicity of the resin dispersion becomes high, its affinity for the offset ink after plate making is undesirably reduced. If it is less than 0.1 mole%, the printing resistance is undesirably reduced.

Organic compounds exhibiting acidity are used as the quaternizing agent. Examples include aliphatic or aromatic carboxylic acids, aliphatic or aromatic halogen-containing compounds, and aliphatic or aromatic sulfonic acids, specifically dimethyl sulfate, methyl chloride and ethyl chloride. Dimethyl sulfate and methyl chloride are preferred.

The C_{1-20} alkyl esters of acrylic or methacrylic acid (iii) contained in the insoluble copolymer may, for

example, be esters of acrylic or methacrylic acid with alcohols, for example n-butanol, isobutanol, n-hexyl alcohol, 2-ethylhexyl alcohol, n-octanol, n-nonyl alcohol, isononyl alcohol, n-decyl alcohol, isodecyl alcohol, n-dodecyl alcohol, n-tridecyl alcohol, n-octadecyl alcohol, n-propanol, isopropanol, ethanol and methanol. Of these C_{4-12} alkyl esters of methacrylic acid are preferred. n-Octyl methacrylate and 2-ethylhexyl methacrylate are especially preferred.

Examples of the C_{3-8} cycloalkyl esters of acrylic or methacrylic acid (iii) contained in the insoluble copolymer are esters of acrylic or methacrylic acid with alcohols such as cyclopropyl alcohol, cycloheptyl alcohol, cyclohexyl alcohol, cyclopentyl alcohol and cyclooctyl alcohol. Cyclohexyl methacrylate is preferred.

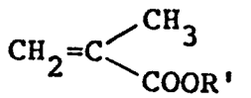
The insoluble copolymer may include at least one C_{1-20} alkyl ester and/or C_{3-8} cycloalkyl ester of acrylic or methacrylic acid (iii). Preferably, the compound (iii) is contained in an amount of 2 to 48% by weight. If the amount exceeds 48% by weight, the image density is reduced or the printing resistance becomes poor. Furthermore, amounts less han 2% by weight are undesirable because the particle diameter of the resin increases and the settling stability of the resin particles is reduced.

The insoluble copolymer may, as required, contain components other than vinyl acetate, the monomer of formula (I) and the C_{1-20} alkyl ester and/or C_{3-8} cycloalkyl ester of acrylic or methacrylic acid within a range which does not adversely affect various properties such as stability, backgrounding or printing resistance.

Examples of the monomer of formula (II) in (iv) contained in the soluble copolymer include methacrylates or acrylates such as n-butyl, isobutyl, n-hexyl, n-octyl, 2-ethylhexyl, n-dodecyl, n-tridecyl, n-octadecyl, n-nonyl, isononyl, n-decyl and isodecyl esters of acrylic or

methacrylic acid, vinyl esters of fatty acids such as vinyl propionate, vinyl butyrate and vinyl Versatate, and vinyl ethers such as vinyl n-butyl ether and vinyl iso-butyl ether.

Preferred monomers of formula (II) are represented by the following formula



[II]

wherein R' represents C_{4-12} alkyl, and 2-ethylhexyl methacrylate and n-octyl acrylate are especially preferred.

If the proportion of the monomer of formula (II) exceeds 95%, the image blurring or the printing resistance is undesirably reduced. If it is less than 15% by weight, the settling stability is undesirably reduced.

Examples of the monomer of formula (III) in (v) contained in the soluble copolymer include C_{3-8} cycloalkyl esters of acrylic or methacrylic acid and gamma-phenyl propyl ester, beta-phenyl ethyl ester and benzyl ester of acrylic or methacrylic acid.

Preferred monomers of formula (III) are C_{3-8} cycloalkyl methacrylates and C_{3-8} cycloalkyl acrylates.

If the proportion of the monomer of formula (III) exceeds 85% by weight, the solubility of the soluble copolymer is reduced to decrease the stability of the resulting dispersion. Proportions of less than 5% by weights are undesirable because the image blurring or the printing resistance is reduced.

The organic mercaptan having at least one thiol group in (vi) contained in the soluble copolymer has 1 to about 4 thiol groups per molecule and 1 to about 12 carbon atoms, preferably 2 to 8 carbon atoms, per thiol group. The organic mercaptan may contain another substituent in addition to the hydrocarbon group. Such a substituent

includes a carboxylic acid group, a hydroxyl group, an ether group, an ester group, a sulfide group, an amino group and an amide group. Examples of useful mercaptans include methylmercaptan, ethylmercaptan, butylmercaptan, octylmercaptan, laurylmercaptan, mercaptoethanol, mercaptopropanol, mercaptobutanol, mercaptoacetic acid, mercaptopropionic acid, thiomalic acid, benzylmercaptan, phenylmercaptan, cyclohexylmercaptan, 1-thioglycerol, 2,2'-dimercaptodiethyl ether, 2,2'-dimercaptodipropyl ether, 2,2'-dimercaptodiisopropyl ether, 3,3'-dimercaptodipropyl ether, 2,2'-dimercaptodiethyl sulfide, 3,3'-dimercaptodipropyl sulfide, 1,11-dimercapto-3,9-dioxa-6-thiaundecane, bis(beta-mercaptoethoxy)methane, bis-(beta-mercaptoethylthio)methane, ethanedithiol-1,2, propanedithiol-1,2, butanedithiol-1,4, 3,4-dimercaptobutanol-1, trimethylolethane tri(3-mercaptopropionate), pentaerythritol tetra(3-mercaptopropionate), trimethylolpropane trithioglycolate and pentaerythritol tetrathioglycolate.

Examples of preferred organic mercaptans are butylmercaptan, octylmercaptan, laurylmercaptan, mercaptoethanol, mercaptopropanol, mercaptobutanol, mercaptoacetic acid, mercaptopropionic acid, benzylmercaptan and phenylmercaptan. Laurylmercaptan, mercaptoethanol, mercaptopropanol, mercaptobutanol, mercaptoacetic acid and mercaptopropionic acid are especially preferred.

The content of the organic mercaptan, as the sulfur content, is preferably 0.03 to 2% by weight based on the soluble copolymer. If it exceeds 2% by weight, the settling stability of the dispersion is undesirably reduced. If it is less than 0.03% by weight, the stabilty of the dispersion on dilution is unsatisfactory, or backgrounding occurs in the developed material.

As required, the soluble copolymer may contain components other than the monomer of formula (II), the monomer of formula (III) and the organic mercaptan within

a range which does not adversely affect various properties such as stability, backgrounding and printing resistance.

The soluble copolymer used in this invention has a molecular weight of preferably not more than 50,000, preferably 3,000 to 30,000, most preferably 5,000 to 25,000. If its molecular weight exceeds 50,000, the stability of the dispersion on dilution tends to be reduced or backgrounding tends to occur in the developed material. If the molecular weight is too low, the stability of the dispersion becomes undesirably poor.

The proportions of the soluble copolymer (B) and the insoluble polymer (A) in the resin dispersion of this invention are not particularly restricted. The resin dispersion contains 5 to 50% by weight, preferably 20 to 50% by weight, more preferably 30 to 40% by weight, of the soluble copolymer and 95 to 50% by weight, preferably 80 to 50% by weight, more preferably 70 to 60% by weight, of the insoluble polymer. If the proportion of the soluble copolymer is less than 20% by weight, the stability of the resulting resin dispersion is reduced undesirably. If it is too large beyond 50% by weight, the image has blurring or a low density, and the printing resistance is reduced.

The dispersed particles in the resin dispersion of this invention have a particle size distribution such that the proportion of particles having a size of not more than 0.5 micron is at least 70%, preferably at least 90%.

The highly insulating hydrocarbon medium contained in the resin dispersion of this invention is an organic solvent having a low dielectric constant and high electrical insulation. Examples of such an organic solvent are n-paraffinic hydrocarbons, iso-paraffinic hydrocarbons, alicyclic hydrocarbons and halogenated aliphatic hydrocarbons. From the standpoint of odors, safety and drying property, paraffinic or alicyclic hydrocarbon media having a boiling point of 150 to 200°C are preferably used.

Generally, the resin dispersion of this invention can be easily produced by performing polymerization of forming the insoluble polymer in a solution of the soluble polymer in the medium. It can also be produced, for example, by separately producing the soluble copolymer and the insoluble polymer, dissolving the two polymers in a common solvent for both, and then adding the solution dropwise to a hydrocarbon medium with stirring.

The particle size distribution of the resin dispersion can be adjusted by varying the ions of the soluble copolymer and the insoluble polymer, or by varying the amount of the C_{1-20} alkyl methacrylate or acrylate (iii) in the insoluble polymer.

Conversion of at least part of the monomer of formula (I) contained in the insoluble polymer into a quaternary ammonium compound may be carried out in a customary manner using a quaternizing agent such as dimethyl sulfate after preparation of the resin dispersion. As an alternative method, prior to the polymerization reaction, the monomer (I) may be quaternized with dimethyl sulfate or methyl chloride by a conventional method.

An electrophotographic liquid developer may be prepared from the resin dispersion of this invention by imparting an electric charge to it after optionally coloring the dispersed resin particles.

A charge controlling agent is used to impart an electric charge to the resin dispersion of this invention. Examples of such a charge controlling agent include zinc naphthenate, manganese naphthenate, copper oleate, cobalt octylate, lecithin, sodium dioctylsulfosuccinate, and aluminum salt of Staybelite rosin.

Nigrosine-type dyes, phthalocyanine-type pigments, oil black, carbon black, etc. are used to color the resin dispersion of this invention.

Best Mode of Practicing the Invention

EXAMPLE 1

A reactor equipped with a stirrer, a refluxing device and a dropping device was charged with 120 g of n-heptane, 40 g of toluene and 4 g of azobisisobutyronitrile. They were heated, and under reflux, a mixture of 130 g of n-octyl methacrylate, 70 g of cyclohexyl methacrylate and 2 g of azobisisobutyronitrile was added dropwise to the heated mixture over 1 hour. After reaction for 1 hour, a mixture of 40 g of toluene and 1.5 g of azobisisobutyronitrile was added over the course of 30 minutes, and the reaction was further carried out for 2 hours. Then, a mixture of 300 g of vinyl acetate and 3 g of benzoyl peroxide was added dropwise over 2.5 hours, and the reaction was carried out for 30 minutes. A mixture of 200 g of n-heptane and 2 g of PEROYL L (a product of Nippon Oils and Fats Co., Ltd.) was added dropwise over 30 minutes, and the reaction was carried out for 20 minutes. After the reaction, a mixture of 12 g of diethylaminoethyl methacrylate, 4 g of n-heptane and 1 g of PEROYL L was added, and after reaction for 1 hour, 1 g of PEROYL L was added. The reaction was further carried out for 2 hours, and 100 g of Isopar G and 0.2 g of dimethyl sulfate were added. The mixture was cooled to give a stable opalescent resin dispersion.

Twenty grams of the resulting resin dispersion, 1.6 g of Bontron N-04 (a product of Orient Chemical Industry Co., Ltd.), 180 g of Isopar G and 1 g of zinc naphthenate were kneaded for 11 hours in a sandmill to obtain a thick developer. It was diluted to 10 times with Isopar G to give a developer.

EXAMPLE 2

The same reactor as used in Example 1 was charged with 125 g of n-octyl methacrylate, 79 g of cyclohexyl methacrylate and 2 g of mercaptoethanol, and the compounds were stirred while introducing air onto the

liquid surface. The mixture was maintained at 80°C for 16 hours, and then the introduction of air was stopped. n-Heptane (35 g) was added, and the mixture was heated, and under reflux, a mixture of 40 g of toluene and 1.5 g of azobisisobutyronitrile was added dropwise over 3 hours. The reaction was continued for 2 hours. The resulting copolymer had a molecular weight of about 15,000. Then, 70 g of n-heptane was added, and under reflux, a mixture of 150 g of vinyl acetate, 25 g of n-octyl methacrylate and 4 g of benzoyl peroxide was added over 2 hours. After reaction for 1 hour, a mixture of 150 g of vinyl acetate, 40 g of n-heptane and 4 g of benzoyl peroxide was added dropwise over 1 hour, and the reaction was carried out for 30 minutes. A mixture of 10 g of dimethylaminoethyl methacrylate, 15 g of ethyl acrylate and 1 g of benzoyl peroxide was then added, and the reaction was carried out for 30 minutes. Furthermore, a mixture of 1 g of PEROYL L and 5 g of n-heptane was added, and the reaction was carried out for 1.5 hours. Then, 10 g of Isopar G was added and the mixture was cooled to less than 10°C, and further 0.1 g of ethyl chloride was added. The resulting dispersion was a very stable emulsion which was slightly transparent and slightly yellowish.

Fifty grams of the resulting resin dispersion, 5.5 g of surface-treated Phthalocyanine Blue, 314 g of Isopar G and 4 g of zinc stearate were kneaded for 24 hours by a ball mill to obtain a thick developer. It was diluted to 10 times with Isopar G to form a developer.

EXAMPLE 3

In the same reactor as in Example 1, 140 g of 2-ethylhexyl methacrylate, 60 g of benzyl methacrylate, 0.4 g of azobisisobutyronitrile, 3 g of mercaptoacetic acid and 35 g of n-hexane were heated to reflux. Under reflux, they were reacted for 2 hours, and then a mixture of 10 g of toluene and 0.3 g of azobisisobutyronitrile was added dropwise over 2 hours. The reaction was further

carried out for 2 hours to give a solution of a copolymer having a molecular weight of about 11,000.

Then, a mixture of 346 g of vinyl acetate, 50 g of 2-ethylhexyl acrylate, 8 g of PERBUTYL O (a product of Nippon Oils and Fats Co., Ltd.) and 150 g of n-heptane was added dropwise to the copolymer solution over 4 hours, and the reaction was carried out for 1 hour. Then, 4 g of PERBUTYL O was added dropwise over 30 minutes, and 20 minutes later, a mixture of 4 g of dimethylacrylamide, 5 g of n-heptane and 1 g of PERBUTYL O was added. Furthermore, 30 minutes later, 1 g of PERBUTYL O as added. The reaction was carried out for 2 hours, and 100 g of Isopar G was added. The mixture was cooled, and then 0.05 g of dimethyl sulfate was added.

The resulting dispersion was a slightly transparent pale brown emulsion having an average particle diameter of 0.2 micrometer.

Isopar G (150 g) was added to 100 g of the resulting resin dispersion, and with stirring, a mixture of 5 g of Oil Black HBB and 20 g of xylene was added dropwise. One gram of aluminum stearate was added and then 10 liters of Isopar G was added to form a developer.

EXAMPLE 4

To the n-octyl methacrylate/cyclohexyl methacrylate copolymer solution obtained in Example 2 were added 70 g of n-hexane, 130 g of Isopar G, 227 g of vinyl acetate, 35 g of n-octyl methacrylate, 21 g of cyclohexyl methacrylate, and 6 g of benzoyl peroxide, and the mixture was reacted under reflux. Three hours later, the mixture became whitened. A mixture of 45 g of n-heptane and 2 g of benzoyl peroxide was added and the reaction was carried out for 1 hour. Then, 24 g of N,N-dimethylaminopropylacrylamide, 30 g of methyl acrylate, 0.4 g of a methyl chloride salt of dimethylaminoethyl methacrylate and 1 g of benzoyl peroxide were added to the mixture, and the reaction was carried out for 1 hour. Furthermore, 1 g of

benzoyl peroxide was added, and the reaction was carried out for 2 hours to form a slightly transparent pale brown emulsion.

A developer was prepared from the resulting resin dispersion by the same method as in Example 2.

COMPARATIVE EXAMPLE 1

A developer was prepared by the same method as in Example 1 except that stearyl methacrylate was used instead of cyclohexyl methacrylate of Example 1.

COMPARATIVE EXAMPLE 2

A developer was prepared in the same way as in Example 1 except that in the polymerization of forming the dispersion, the mixture of 12 g of diethylaminoethyl methacrylate, 4 g of n-heptane and 1 g of PEROYL L was not added.

COMPARATIVE EXAMPLE 3

A developer was prepared in the same way as in Example 2 except that the amount of dimethyl sulfate (0.1 g) after the polymerization of forming the dispersion was changed to 1 g.

COMPARATIVE EXAMPLE 4

A developer was prepared in the same way as in Example 3 except that after the polymerization of forming the dispersion, dimethyl sulfate was not added.

Using each of the developers obtained as above, an image was formed on an offset master electrostatic recording sheet coated with zinc oxide, followed by an etching treatment. Then, printing was carried out with a commercial offset ink using the offset master.

Table 1 summarizes the compositions of the resin dispersions obtained in Examples 1 to 4 and Comparative Examples 1 to 4, and Table 2 shows the results of the printing test.

Table 1

	Insoluble copolymer (wt.%)			Quaternizing agent	Soluble copolymer (wt.%)		Organic mercaptan
	Monomer of (A), (i) in claim 1	Monomer of (A), (ii) in claim 1	Monomer of (A), (iii) in claim 1	Monomer of (A), (ii) in claim 1 (mole%)	Monomer of formula(II)	Monomer of formula (III)	Soluble copolymer (sulfur, wt.%)
Example 1	96.2	3.8	0	2.4	65	35	0
2	85.7	2.9	11.4	2.4	62.5	37.5	0.4
3	86.5	1.0	12.5	1.0	70	30	0.5
4	67.4	7.1	25.5	1.3	62.5	37.5	0.4
Comparative Example 1	96.2	3.8	0	2.4	100	0	0
2	100	0	0	∞	65	35	0
3	85.7	2.9	11.4	10	62.5	37.5	0.4
4	86.5	1.0	12.5	0	70	30	0.5

Table 2

	Plate image			Print	
	Density 1)	Blurring 2)	Printing resistance 3)	Clearness 4)	Back-grounding 5)
Example 1	3	4	4	4	4
2	4	4	5	5	5
3	5	4	4	5	5
4	3	4	5	4	5
Comparative Example 1	3	1	4	1	1
2	3	4	1	4	3
3	1	2	5	1	2
4	5	4	1	5	5

1) The density obtained with Example 1 was taken as standard (3), and the number was increased with increasing density.

2) Blurring of the image was evaluated on a scale of five points as follows:

5: No blurring
4: Slight blurring
3: Some blurring
2: Blurring occurred
1: Much blurring

3) Using an etched plate having formed thereon an image to be printed as a master sheet, printing was carried out on high-quality paper with a commercial offset ink. Evaluated by the number of prints obtained until images of the fine dots disappeared.

5: more than 5,000
4: 4,000 to 5,000
3: 3,000 to 4,000
2: 2,000 to 3,000
1: more than 2,000

4) Evaluated by the density, blurring at the edge of the image area, and the clearness of the fine dots in a print obtained by the printing resistance test

5: The density was high, no image blurring and the fine dots were clear.
4: Slight blurring was noted in the printed portion in dark color.
3: Some blurring was noted in the edge of the printed portion.
2: The image generally blurred, and the fine dots were slightly obscure.
1: The iamge blurred or became low in density, or the fine dots adhered to each other to give a solid.

5) Five printed papers obtained by the printing resistance test were superimposed with the image areas

being in registration with each other. The non-image areas were compared with the same number of non-printed papers, and the state of smudging was evaluated.

5: No difference was noted even when they were superimposed.

4: A slight difference was noted.

3: Some difference was noted.

2: A difference was noted.

1: A very large difference was noted.

EXAMPLE 5

The same reactor as used in Example 1 was charged with 140 g of 2-ethylhexyl methacrylate, 60 g of benzyl methacrylate, 0.4 g of azobisisobutyronitrile, 3 g of mercaptoacetic acid and 35 g of n-hexane, and they were heated to reflux. Under reflux, the reaction was carried out for 2 hours, and then a mixture of 10 g of toluene and 0.3 g of azobisobutyronitrile was added dropwise over 2 hours. Furthermore, the reaction was carried out for 2 hours to obtain a solution of a copolymer having a molecular weight of about 11,000.

Then, a mixture of 2,240 g of vinyl acetate, 560 g of 2-ethylhexyl acrylate, 56 g of PERBUTYL O (a product of Nippon Oils and Fats Co., Ltd.) and 1050 g of n-heptane was added dropwise over 4 hours, and the reaction was carried out for 1 hour. Then, 28 g of PERBUTYL O Was added dropwise over 30 minutes, and 20 minutes later, a mixture of 28 g of dimethylacrylamide, 35 g of n-heptane and 7 g of PERBUTYL O was added, and the reaction was carried out for 2 hours. Isopar G (350 g) was added to the reaction mixture. The mixture was cooled and then 0.35 g of dimethyl sulfate was added.

The resulting dispersion was a slightly transparent pale brown emulsion having an average particle diameter of 0.2 micrometer.

Isopar G (150 g) was added to 100 g of the resulting dispersion, and with stirring, a mixture of 5 g

of Oil Black HBB and 20 g of xylene was added dropwise. Then, while adding 1 g of aluminum stearate, 10 liters of Isopar G was added to form a developer. The values of the resulting resin dispersion which correspond to columns 2 to 8 of Table 1 were as follows:

Components of the insoluble copolymer (wt. %)
Monomer (i) in (A) in claim 1: 79.2
Monomer (ii) in (A) in claim 1: 1.0
Monomer (iii) in (A) in claim 1: 19.8
Quaternizing agent: Monomer (ii) in (A) in claim 1 (mole%) 1.0
Components of the soluble copolymer (wt.%)
Monomer of formula (II): 70
Monomer of formula (III): 30
Organic mercaptan: soluble copolymer component (sulfur content, wt.%): 0.5

The printing test was conducted by using the resulting developer, and the results were as follows:

Density: 4
Blurring: 4
Printing resistance: 4
Clearness: 5
Backgrounding: 4

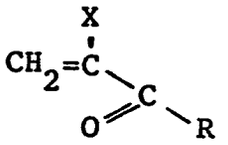
Possibility of Utilization in Industry

Since the resin dispersion of this invention has very good stability, an electrophotographic liquid developer for offset masters prepared from it is very stable even when formed into a developer bath by diluting it to about 160 times, and a phenomenon of formation of a large amount of a precipitate or a gel-like flocculated mass does not occur. In offset printing, no image blurring (blurring of contours) or backgrounding occurs, and the developer has such an excellent printing resistance that even after printing 5,000 copies, the desired clear image can be obtained.

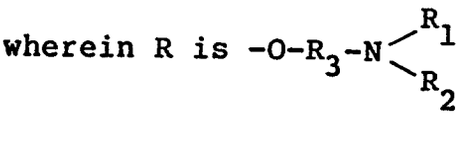
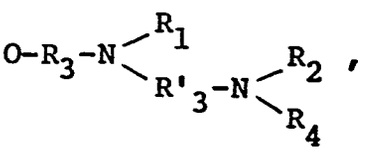
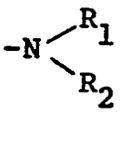
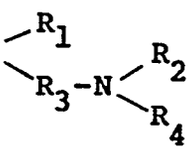
SCOPE OF CLAIM FOR PATENT

1. A resin dispersion suitable as an electrophotographic liquid developer for offset masters, said dispersion comprising in a highly insulating hydrocarbon medium,

(A) a copolymer substantially insoluble in said medium and containing (i) 20 to 99.5% by weight of vinyl acetate, (ii) 0.5 to 12% by weight of a monomer of the formula

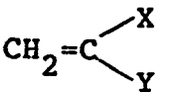


(I)

wherein R is  ,  ,  or  , in which R_1, R_2 and R_4, independently from each other, represent hydrogen, C_{1-6} alkyl, or alkoxyalkyl containing 1 to 4 carbon atoms in each alkyl moiety, R_3 and R'_3, independently from each other, represent C_{1-4} alkylene, and X represents hydrogen or methyl,

and (iii) 0 to 79.5% by weight of a C_{1-20} alkyl ester and/or a C_{3-8} cycloalkyl ester of acrylic or methacrylic acid (provided that the sum of (i), (ii) and (iii) is 100% by weight), with at least part of said monomer of formula (I) being quaternized in its amino group with a quaternizing agent to convert it into a quaternary ammonium compound, and

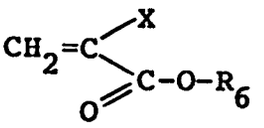
(B) a copolymer substantially soluble in said medium and containing (iv) 95 to 15% by weight of a monomer of the formula



(II)

wherein X is as defined above, Y represents $-COOR_5$, $-OCOR_5$ or $-OR_5$, and R_5 represents C_{4-20} alkyl,

(v) 5 to 85% by weight of a monomer of the formula



(III)

wherein X is as defined above, and R_6 represents C_{3-8} cycloalkyl or aralkyl containing 1 to 3 carbon atoms in the alkyl moiety,

(provided that the sum of (iv) and (v) is 100% by weight), and (vi) 0 to 2% by weight (in terms of sulfur content) of an organic mercaptan having at least one thiol group (provided that the sulfur content is the sulfur content of the soluble copolymer in % by weight).

2. The resin dispersion set forth in claim 1 wherein the soluble copolymer contains the organic mercaptan in an amount corresponding to a sulfur content of 0.03 to 2% by weight.

3. The resin dispersion set forth in claim 2 wherein the amount of the quaternizing agent used is 0.1 to 5 mole% based on the monomer of formula (I).

4. The resin dispersion set forth in any one of claims 1 to 3 wherein the molecular weight of the soluble copolymer is not more than 50,000.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/JP86/00340

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl[4] G03G9/12

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
IPC	G03G9/12

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category*	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
A	JP, A, 53-54029 (Philip. A. Hunt. Chemical. Corp.) 17 May 1978 (17. 05. 78) (Family: none)	1 - 4
A	JP, A, 59-83174 (Mitsubishi Paper Mills Ltd.) 14 May 1984 (14. 05. 84) & DE, A, 3,339,662	1 - 4

* Special categories of cited documents: [15]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2]	Date of Mailing of this International Search Report [2]
September 22, 1986 (22.09.86)	September 29, 1986 (29.09.86)
International Searching Authority [1]	**Signature of Authorized Officer [20]**
Japanese Patent Office	