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(54) IMPROVEMENTS RELATING TO ELECTROPHORETIC DEVELOPERS

(71) We, AGFA GEVAERT, a naamloze vennootschap organised under the laws of Belgium, of Septestraat 27, B 2510 Mortsel, Belgium do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

The present invention relates to liquid developers suitable for use in electrophoretic development of electrostatic charge patterns.

An electrostatographic process known as electrophotography comprises the steps of electrostatically charging in the dark a photoconductive surface and image-wise exposing said surface, whereby the irradiated areas become discharged in accordance with the intensity of radiation thus forming a latent electrostatic image. The formation of a visible image proceeds by supplying to the image-wise charged material a finely divided electroscopic material known as "toner". The toner is image-wise electrostatically attracted or repelled so that a direct or reversal toner image of the pattern represented by the charge density distribution is obtained. The toner image may be fixed to the surface of the photoconductor or transferred to another surface and fixed thereon.

Instead of forming the electrostatic image by the steps described above it is also possible to charge directly a dielectric material in image configuration, e.g. with a charged stylus, or through photo-electron emission or ionography.

Historically, a one-component dry powder toner was first used for developing electrostatic images. Other development processes, known at present as cascade, fur brush, powder cloud, magnetic brush, and liquid electrophoretic development were introduced.

Developers of the electrophoretic type initially comprised a simple dispersion of a pigment but no binder. It was later proposed, e.g. by Metcalfe and Wright, J.Oil Colour Chem. Ass., 39 (1956) 851-853, to use liquid developers incorporating resins and control agents. The resultant images are then made of so-called "self-fixing" toners.

In liquid developers comprising coloured toner particles suspended in an insulating carrier liquid, the volume resistivity of the liquid is preferably in excess of 10^9 Ohm.cm and its dielectric constant is below 3. The suspended toner particles, which usually comprise finely divided pigments (which expression includes dyes in pigment form), obtain an electric charge of a definite polarity by the so-called charge control agent(s) and develop the latent image under influence of the charge of the latent electrostatic image.

The charging of the toner particles can be achieved by the addition of oil-soluble ionogenic substances, e.g. metallic salts of organic acids with sufficiently long aliphatic chains. By predominant adsorption of one ionic species the particles receive a net charge whose amount can be regulated simply by changing the additive concentration. The polarity is controlled by the appropriate choice of ionogenic substance.

The resin in an electrophoretic pigment-resin toner combination is used primarily to provide a good dispersion stability and adhesion of dried toner to its final support e.g. a receiving sheet of paper, resin, or metal.

The transfer of the still wet toner image to a receptor paper is of interest e.g. in plain paper electrophotography in which the photoconductor member, e.g. the selenium drum, after transfer of the toner image is reused for recharging and information-wise exposure.

The transfer of the toner image e.g. from a conventional zinc oxide paper to a printing plate base, is of particular interest in the economical manufacture of planographic printing plates.

Many liquid developers when used in toner transfer systems yield transfer images of poor density and form a toner deposit that is easily rubbed off and is not fit for forming a wear-resistant ink accepting pattern in planographic printing.

In the production of transfer images on planographic printing supports, e.g. aluminium sheets or plates, the transferred toner images should possess a good water resistance, tenacious adherence, and abrasion resistance as well as a satisfactory resolution.

Accordingly, there is a need in the art for resins for liquid toner developer compositions, which provide the above defined properties to the toner. There is a further need for such liquid toner developer compositions, which retain their charge and dispersion stability for extended periods of time and which do not deteriorate with age or upon exposure to the atmosphere.

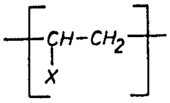
Therefore, it is an object of the present invention to provide stable liquid toner developer compositions that are capable of producing dense toner images that can be transferred to produce excellent long run planographic printing masters as a result of their strong erasure-resistance.

It is another object of the present invention to provide liquid toner developer compositions containing synthetic resin constitutents giving the toner such desired properties in a reproducible way.

In accordance with the present invention a liquid developer composition is provided that is suitable for use in developing electrostatic charge patterns, which composition contains in an electrically insulating non-polar carrier liquid a dispersed particulate colouring substance, one or more charge-control substances, a copolymer (I) in a weight ratio of copolymer (I) to colouring substance between 1:1 and 9:1 and a copolymer (II) in a weight ratio of copolymer (II) to colouring substance between 0.5:1 and 5:1,

-said copolymer (I) being a copolymer consisting of 50 to 90 mole% of recurring units of the following formula(A)

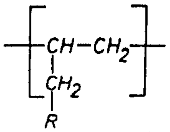
(A)



$$\left[-\underset{\substack{| \\ X}}{CH}-CH_2- \right]$$

wherein X is phenyl or alkylphenyl and from 10 to 50 mole% of recurring units of the following formula (B)

(B)



$$\left[-\underset{\substack{| \\ CH_2 \\ | \\ R}}{CH}-CH_2- \right]$$

wherein R is a hydroxyl group or is a group resulting from the esterification of hydroxyl by means of a C_{12}-C_{20} aliphatic acid with the proviso that the copolymer (I) contains at least 0.5% by weight of free hydroxyl groups, and said copolymer (II) being a copolymer:

(a) a copolymer of at least one C_{12}-C_{20} alkyl ester of methacrylic acid (X) and the n-butyl or isobutyl ester of methacrylic acid (Y)

(b) a copolymer of X, Y and up to 70 % by weight of styrene or a vinyl toluene, or,

(c) a copolymer of X, Y and up to 0.4 % by weight of methacrylic acid,

the weight ratio of X to Y in this copolymer being between 15:85 and 50:50.

Particularly suitable copolymers (I) have a hydroxyl content of 5.4 to 6 % by weight and a molecular weight in the range of 1500 to 2400. Such copolymers are marketed by Monsanto under the trade names RJ 100 and RJ 101 respectively.

The solubility of copolymer (I) in the non-polar liquid is easily controlled by varying the molar ratio of (A) and (B). The non-polar moiety (A) increases the solubility in the developer liquid. The presence of an esterified group in structural unit (B) tends to increase further the solubility of copolymer (I) in said liquid.

The presence of free hydroxyl in the polar moiety (B) makes the copolymer (I) precipitate onto the dispersed particulate colouring substance, e.g. carbon black, so that a good adherence is obtained on an aluminium support later on.

The preparation of allyl alcohol-styrene copolymers (I) is described by Schildknecht in "Allyl Compounds and their Polymers" Vol.28, p.204-206, (1973) J. Wiley & Sons, Interscience Publishers.

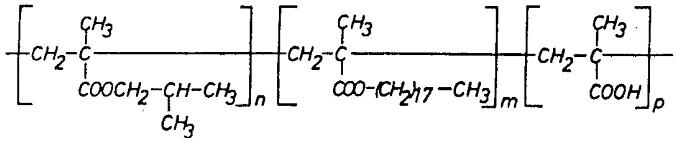
The procedure for preparing partial fatty acid esters of styrene-allyl alcohol copolymers either by molten phase of an azeotropic cooking procedure is described in Technical Service Bulletin "RJ-100" for solvent-based vehicles (1963) of Monsanto.

Preferred copolymers (II) have a molecular weight of at least 40,000. Examples thereof are listed in Table 1.

Table 1

Copolymer (II) no.	Trade name	Average molecular weight
1	NEOCRYL B702	70,000
2	NEOCRYL B707	100,000
3	PLEXOL 618	300,000

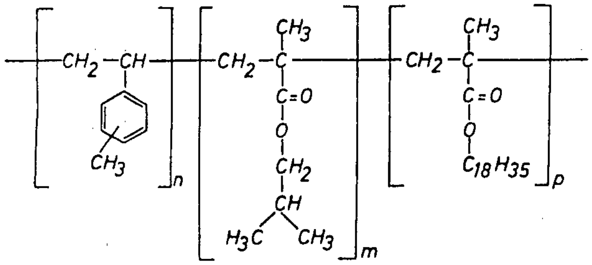
NEOCRYL B702 is a trade mark of Polyvinyl Chemie Holland, Waalwijk, Netherlands, for a copolymer of isobutyl methacrylate, stearyl methacrylate, and methacrylic acid. NEOCRYL B702 has the following structure :



$$\left[-CH_2-\underset{COOCH_2-\underset{CH_3}{CH}-CH_3}{\overset{CH_3}{C}}-\right]_n\left[-CH_2-\underset{COO-(CH_2)_{17}-CH_3}{\overset{CH_3}{C}}-\right]_m\left[-CH_2-\underset{COOH}{\overset{CH_3}{C}}-\right]_p$$

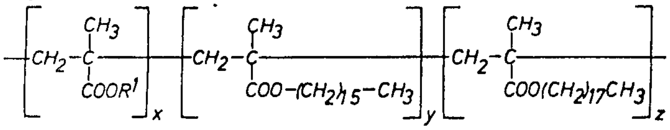
wherein:
n = from 75 to 85 % by weight,
m = 15 to 25% by weight,
p = about 0.2% by weight.

NEOCRYL B707 is a trade mark of Polyvinyl Chemie Holland, Waalwijk, Netherlands, for a copolymer of m-and p-vinyltoluene, isobutyl methacrylate, and stearyl methacrylate corresponding to the following formula :



wherein:
n = 60% by weight,
m = 20% by weight,
p = 20% by weight.

PLEXOL 618 is a trade mark of Rohm & Haas, Philadelphia, Pa., USA for a copolymer having the following structure:



$$\left[-CH_2-\underset{COOR^1}{\overset{CH_3}{C}}-\right]_x\left[-CH_2-\underset{COO-(CH_2)_{15}-CH_3}{\overset{CH_3}{C}}-\right]_y\left[-CH_2-\underset{COO(CH_2)_{17}CH_3}{\overset{CH_3}{C}}-\right]_z$$

wherein:
R^1 = n-butyl,
x = 56% by weight,
y = 26 % by weight,
z = 18 % by weight.

The insulating liquid used as carrier liquid in the liquid developer according to the invention may be any kind of nonpolar, fat-dissolving solvent. The insulating liquid used as carrier liquid preferably has a volume resistivity of at least 10^9 Ohm.cm and a dielectric constant of less than 3. Said liquid preferably is a hydrocarbon solvent, e.g. an aliphatic hydrocarbon such as hexane, cyclohexane, iso-octane, heptane or isododecane, a fluorocarbon or a silicone oil. Thus, the insulating liquid is e.g. isododecane or a commercial petroleum distillate, e.g. a mixture of aliphatic hydrocarbons preferably having a boiling range between 150°C and 220°C such as the ISOPARS G, H, K and L (trade marks) of Exxon and SHELLSOL T (trade mark) of the Shell Oil Company.

The colouring substance used in the toner particles may be any inorganic pigment (said term including carbon) or solid organic dyestuff pigment commonly employed in liquid electrostatic toner compositions. Thus, for example, use can be made of carbon black and analogous forms thereof, e.g. lamp black, channel black, and furnace black, e.g. RUSS

PRINTEX 140 GEPERLT (trade mark of Degussa, Frankfurt/M, W. Germany).

Typical solid organic dyestuffs are so-called pigment dyes, which include phthalocyanine dyes, e.g. copper phthalocyanines, metal-free phthalocyanine, azo dyes, and metal complexes of azo dyes.

The following dyes in pigment form are given for illustration purposes only : FANAL-ROSA B Supra Pulver (trade mark of Badische Anilin- & Soda-Fabrik AG, Ludwigshafen, Western Germany), HELIOGENBLAU LG (trade mark of BASF for a metal-free phthalocyanine blue pigment), MONASTRAL BLUE (a copper phthalocyanine pigment, C.I. 74,160). HELIOGENBLAU B Pulver (trade mark of BASF), HELIOECHTBLAU HG (trade mark of Bayer AG, Leverkusen, Western Germany, for a copper phthalo-cyanine C.I. 74,160), BRILLIANT CARMINE 6B (C. I. 18,850), and VIOLET FANAL R (trade mark of BASF, C.I. 42,535).

Typical inorganic pigments include black iron (III) oxide and mixed copper(II) oxide/chromium(III) oxide/iron(III) oxide powder, milori blue, ultramarine cobalt blue, and barium permanganate. Further are mentioned the pigments described in the French Patent Specifications 1,394,061 and 1,439,323.

Preferred carbon black pigments are marketed by Degussa under the trade mark PRINTEX. PRINTEX 140 and PRINTEX G are preferably used in the developer composition of the present invention. The characteristics of said carbon blacks are listed in the following Table 2.

Table 2

	PRINTEX 140	PRINTEX G
origin	channel black	furnace black
density	1.8 g.cm^{-3}	1.8 g.cm^{-3}
grain size before entering the developer	29 nm	51nm
oil number (g of linseed oil adsorbed by 100 g of pigment)	360	250
specific surface (sq.m per g)	96	31
volatile material % by weight	6	2
pH	5	8
colour	brownish-black	bluish-black

As colour corrector for the PRINTEX (trade mark) pigments minor amounts of copper phthalocyanine may be used, e.g. from 1 to 20 parts by weight with respect to the carbon black.

For a given charge density of the charge-carrying surface the maximum development density attainable with toner particles of a given size is determined by the charge/toner particle mass ratio, which is determined substantially by the amount of employed substance conctrolling the electrical polarity.

In contrast with dry toners the liquid-suspended toner particles acquire normally their negative or positive charge from a chemical dissociation reaction on the toner particle surface and the introduction of a charged species in the carrier liquid to form the counterion. The principal charging mechanisms operating with a dissociation reaction are described, e.g., by Robert B. Comizolli et al. in Proceedings of the IEEE, Vol. 60, No. 4, April 1972, p. 363-364.

So, a liquid developer composition according to the present invention includes at least one substance (called "charge control" agent or substance), which influences or is responsible for electrical charging of the toner. The charge control substance(s) may have positive or negative charging effect. Mostly oil-soluble ionogenic substances (surfactants), e.g. metallic salts or organic acids with an aliphatic chain containing at least 6 carbon atom are used for that purpose. By predominant adsorption of one ionic species the toner particles receive a net charge, whose amount can be regulated by changing the additive concentration. In this way the sensitivity of the toner (i.e. deposited mass per surface charge) can be controlled. The polarity can be determined by appropriate choice of the surfactant. For example, a suspension of carbon black in liquid isoparaffins becomes negatively charged by overbased calcium petroleum sulphonate having a total base number (hereinafter defined) of at least 2 and positively charged by calcium diisopropyl salicylate. Mixtures of different charge control agents can be used. For example, a mixture of different charge control agents having opposite charging effects can be used so that the strength of the charge on the toner or the polarity thereof can be adjusted by varying the ratio between the different agents (see UK Patent applications nos. 1,411,287; 1,411,537 and 1,411,739). Particularly suitable positively working charge control substances are described in the United Kingdom Patent Specification 1,151,141. These substances called charge control agents are bivalent or trivalent metal salts of :

(a) a monoester or diester of an oxyacid derived from phosphorus,

(b) an oxyacid derived from phosphorous and containing one or two organic groups linked to the phosphorus atom by a carbon atom, or

(c) an oxyacid derived from phosphorus and containing an ester group and an organic group linked by a carbon atom to the phosphorus atom, said organic group being aliphatic, cycloaliphatic, or aromatic.

The organic group preferably comprises a chain of at least 4 carbon atoms, most preferably from 10 to 18 carbon atoms and such chain may be substituted and/or interrupted by hetero-atom(s), e.g. oxygen, sulphur, or nitrogen atom(s).

Particularly good results are obtained with the zinc salts. However, other salts may also be used, e.g. salts of magnesium, calcium, strontium, barium, iron, cobalt, nickel, copper, cadmium, aluminium, or lead.

The solubility in the electrically insulating carrier liquid of such metal salts can be prompted by the presence of one or more organic groups with branched structure, e.g. branched aliphatic groups, such as a 2-butyl-octyl group.

Other particularly suitable positively working charge control agents that are of special interest in the production of an electrophoretic developer with low charge/toner particle mass ratio are described in the United Kingdom Patent Application No. 38,068/75 (Serial No. 1571787). That application discloses developer compositions, which contain as control agent a metal alkyl sulphonate whose metal ion is a bivalent metal ion selected from zinc (II), lead (II), cadmium (II), and copper (II) or is a trivalent metal ion e.g. iron (III) or chromium (III) of group VIB or VIII of the Periodic Table of the Elements according to pages 448-449 of "Handbook of Chemistry and Physics", Editor in Chief: Charles D Hodgman, 42nd Edition, published by The Chemical Rubber Publishing Co. Cleveland, Ohio, United States of America, and in which the sulphonate group is present directly on an alkyl chain containing at least 6 carbon atoms in straight line. When a said sulphonate is used as a charge control agent in a developer composition according to the present invention, the sizes of the toner particles and the amount in which said sulphonate is present may (as described in the aforesaid earlier application 38068/75) be such that the toner can develop up to an optical density of at least 0.8, a charge pattern possessing a charge level corresponding to 50 V for a capacitance of 1.5×10^{-11} $F.cm^{-2}$. A suitable amount of the sulphonate for a given toner developer can easily be determined by simple tests. By using a said metal alkyl sulphonate as charge control agent the specified results can be achieved with toner particles of a size commonly used in the electrophotographic art, e.g., with toner particles sizing in the range of 0.2 μm to 2μm. As disclosed in said application an additional charge control agent can be used in conjunction with the metal alkyl sulphonate. A useful amount of these positively charging substances is in the range of 0.5 to 5 % by weight with respect to the dispersed colouring substance, e.g., carbon black.

Particularly suitable negatively working charge control agents are described in United Kingdom Patent Application No. 38023/76 (Serial No.). That application discloses developer compositions, which contain as control agent an organic ionic surfactant which is an oil-soluble hydrocarbon sulphonate of magnesium, calcium, or barium, the sulphonate having an average molecular weight of at least 800, and a total base number (TBN) of at least 2. The expression "total base number" denotes the quantity of acid, expressed in terms of the equivalent number of milligrams of potassium hydroxide, that is required to neutralise a 1 g sample of the surfactant. A useful amount of these negatively charging substances is in the range of 1 to 40% by weight with respect to the dispersed toner.

A liquid developer composition according to the present invention can be prepared by using dispersing and mixing techniques well known in the art. It is conventional to prepare by means of suitable mixers, e.g. kneading apparatus, a 3-roll mill, ball mill, colloid mills, high speed stirrers, a concentrate of e.g. 15 to 80% by weight of the solid materials selected for the composition in the insulating carrier liquid and subsequently to add further insulating carrier liquid to provide the liquid toner composition ready for use in the electrostatic reproduction process. It is generally suitable for a ready for use electrophoretic liquid developer to incorporate the toner in an amount between 1 g and 20 g per litre, preferably between 2 g and 10 g per litre. The copolymers can be applied as a pre-coating to the pigment particles prior to their use in making up the developer or can be introduced as a separate ingredient in the liquid and allowed to adsorb onto the pigment particles. It is preferable to precoat the colouring substance with copolymer (I) and to add in the presence of the charge-control agent copolymer (II), which offers a particularly high stability to the toner.

The electrophoretic development may be carried out by using any known electrophoretic development technique or device. The field of the image to be developed may be influenced by the use of a development electrode. The use of a development electrode is of particular value in the development of continuous tone images. When no development electrode is used, the developed image may exhibit exaggerated density gradients, which may be of interest for certain purposes in graphic arts.

The charge pattern to be developed may be obtained according to any known electrostatographic technique, which includes direct image-wise charging of a dielectric, e.g. by means of a charged stylus through photoelectron emission or ionography or image-wise discharging of a photoconductor medium, e.g. a selenium drum or photo-conductive zinc oxide sheet or plate. Toner transfer from a toner image still being wet proceeds e.g. by electrophoresis. A description of this technique is presented in the published German Patent Applications 2,144,066 and 2,147,646 filed by Canon, 2 and 9 September 1971 respectively.

A planographic printing master obtained by transfer of toner according to the present invention on an aluminium plate forms after fixing by heat, a very robust printing image that can yield printing runs of 50,000 to 100,000 prints with good resolution (about 60 line pairs per cm).

Planographic aluminium printing plates are made fatty ink-repellent and highly water-accepting in the areas not covered by toner according to known wetting techniques, e.g. by treating the plate carrying the toner image with an aqueous solution containing phosphoric acid. Suitable treating liquids for that purpose are described, e.g., in the United States Patent Specification 3,300,306 under the wording "lithographic preparation".

The following examples illustrate the present invention. The ratios and percentages are by weight unless otherwise indicated.

Example 1

Preparation of the liquid toner developer with positively charged toner particles

200 g of the styrene-allyl alcohol copolymer RJ 100 (trade name) resin (average molecular weight 1600) and 100 g of PRINTEX G carbon black (trade name) were introduced in a kneading apparatus type LILIPUT 030 C.N. (trade mark) sold by Meili (Switzerland).

The kneading apparatus was heated with circulating silicone oil at 110°C. After 2 h of kneading, the mass was cooled, broken, and ground in a grinding apparatus IKA model A 10 (sold by Janke & Kunkel, W. Germany) so as to obtain a fine powder of carbon black precoated with RJ 100 resin having a particle diameter of about 50 to 100 μm.

A liquid toner was prepared by milling the following ingredients for 15 h in a vibratory ball mill :

- 42 g of carbon black precoated with RJ 100 (trade mark) resin
- 42 g of a 30% by weight solution of NEOCRYL B 702 (trade mark) in ISOPAR G (trade mark of Exxon for an aliphatic hydrocarbon having a boiling range of 160-175°C and a Kauri-butanol (KB) value of 27)
- 14 ml of a 2% (weight/volume) solution of zinc mono-2-butyl-octyl phosphate in isododecane
- 150 ml of isododecane.

The above toner had a particle diameter of 0.40 μm and a very good stability and shelf-life in the toner concentrate form as well as in the development concentration.

Development and Transfer

7.5 ml of the above concentrated liquid developing composition were diluted with 1 litre of isododecane, which yield a stable positive working electrophoretic developer.

An electrostatic image formed on a conventional electrophotographic recording element, i.e. paper coated with photoconductive zinc oxide dispersed in a resinous binder, which was negatively charged and image-wise exposed to light, was developed with the developer obtained.

The transfer of the electrophoretically deposited toner proceeded by applying a negative voltage of 3 kV to a metal roll, which was kept in close ohmic contact with the rear side of an aluminium sheet acting as the receiving material which was kept with its front side in close contact with the wet image on the photoconductor.

After toner transfer by electrophoresis, the image-wise deposited toner particles were fixed on the aluminium by heating the sheet at 120°C for 20 s.

The transferred toner image was of excellent quality with respect to abrasion resistance and image resolution. The non-image areas of the aluminium plate were hydrophilized in a known way e.g. by means of an aqueous phosphoric acid solution so as to obtain an electrophotographic offset master.

The resolution of this master was about 60 line pairs per cm and more than 50,000 prints of high quality were made on a conventional offset machine.

Example 2

Example 1 was repeated but instead of using RJ 100 (trade name) as coating copolymer for the carbon black, RJ 101 (trade name) being a styrene-allyl alcohol copolymer with average molecular weight (about 1700) was used. The same good results as in Example 1 were obtained.

Example 3

Preparation of a liquid toner developer with negatively charged toner particles

A liquid toner dispersion was prepared by milling in a vibratory ball mill the following ingredients for 15 h :

- 42 g of carbon black precoated with RJ 100 (trade mark) resin as in Example 1,
- 42 g of a 30 % solution of Neocryl B702 (trade mark) in Isopar G (trade mark)
- 14 ml of a 20% (weight/volume) solution of TLA 414 (trade mark of Texaco for an oil-soluble calcium hydrocarbon sulphonate with a total base number hereinbefore defined of 400)
- 150 ml of isododecane.

The thus obtained toner dispersion contained negatively charged toner. The dispersion had a very good stability and shelf-life in the toner concentrate form as well as in the development concentration. The latter concentration was obtained by diluting 7.5 ml of the above toner concentrate with 1 litre of isododecane.

Development and transfer

An electrostatic image formed on a selenium drum, which was positively charged and image-wise exposed to light, was developed with the negatively charged developer.

To transfer the toner particles of the obtained image onto plain paper a positive voltage of 3 kV was applied to the rear side of the paper, which was used as receiving material. The transferred toner particles were fixed by heating the sheet at 120°C for 20 s or by flash-exposure.

The image obtained had a high density and good sharpness.

Example 4

Preparation A

200 g of RJ 100 (trade mark) were melt-kneaded until a homogeneous dispersion of carbon black in the polymer mass was obtained.

Preparation B

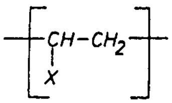
100 g of RJ 100 (trade mark) and 100 g of RJ 100 (trade mark), which had been esterified with lauric acid so as to contain still 0.74 % of hydroxyl groups, and 100 g of PRINTEX G (trade mark) were melt-kneaded until homogeneous dispersion of carbon black was obtained.

The carbon black precoated with resin as described in preparations A and B was used for preparing toner dispersions in the way described in Example 1 or 3.

WHAT WE CLAIM IS:-

1. A liquid developer composition suitable for use in developing electrostatic charge patterns, which composition contains in an electrically insulating non-polar carrier liquid a dispersed particulate colouring substance, one or more charge control substances, a copolymer (I) in a weight ratio of copolymer (I) to colouring substance between 1:1 and 9:1 and a copolymer (II) in a weight ratio of copolymer (II) to colouring substance between 0.5:1 and 5:1, said copolymer (I) being a copolymer consisting of 50 to 90 mole % of recurring units of the following formula (A)

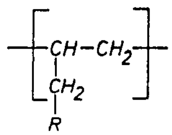
(A)



$$\left[-\underset{X}{CH}-CH_2- \right]$$

wherein X is phenyl or alkylphenyl, and from 10 to 50 mole % of recurring units of the following formula (B)

(B)



$$\left[-\underset{\underset{R}{CH_2}}{CH}-CH_2- \right]$$

wherein R is a hydroxyl group or is a group resulting from the esterification of hydroxyl by means of a C_{12}-C_{20} aliphatic acid with the proviso that the copolymer (I) contains at least 0.5 % by weight of free hydroxyl groups, and said copolymer (II) being:

(a) a copolymer of at least one C_{12}-C_{20} alkyl ester of methacrylic acid (X) and the n-butyl or isobutyl ester of methacrylic acid (Y)

(b) a copolymer of X, Y and up to 70 % by weight of styrene or a vinyl toluene, or

(c) a copolymer of X, Y and up to 0.4 % by weight of methacrylic acid,

the weight ratio of X to Y in this copolymer being between 15:85 and 50:50.

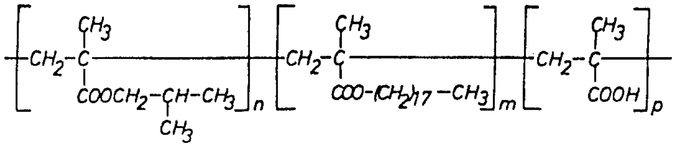
2. A liquid developer composition according to claim 1, wherein the colouring substance has been precoated with the copolymer (I).

3. A liquid developer composition according to claim 1 or 2, wherein the hydroxyl

content of the copolymer (I) is from 5.4 to 6% by weight and the copolymer (I) has a molecular weight in the range of 1500 to 2400.

4. A liquid developer composition according to any of the claims 1 to 3, wherein the copolymer (II) has a molecular weight of at least 40,000.

5. A liquid developer composition according to claim 4, wherein the copolymer (II) has the following structure :



$$\left[-CH_2-\overset{CH_3}{\underset{COOCH_2-\underset{CH_3}{CH}-CH_3}{C}}-\right]_n\left[-CH_2-\overset{CH_3}{\underset{COO-(CH_2)_{17}-CH_3}{C}}-\right]_m\left[-CH_2-\overset{CH_3}{\underset{COOH}{C}}-\right]_p$$

wherein : n = from 75 to 85% by weight
m = 15 to 25 % by weight
p = about 0.2 % by weight.

6. A liquid developer composition according to any of the claims 1 to 5, wherein the carrier liquid has a volume resistivity of at least 10^9 Ohm.cm and a dielectric constant of less than 3.

7. A liquid developer composition according to claim 6, wherein the carrier liquid is an aliphatic hydrocarbon.

8. A liquid developer composition according to any of the preceding claims, wherein the colouring substance is carbon black.

9. A liquid developer composition according to any of the preceding claims, wherein there is a said charge-control substance, which offers a positive charge to the dispersed particulate substance.

10. A liquid developer composition according to any of the claims 1 to 8, wherein there is a said charge-control substance which offers a negative charge to the dispersed particulate substance.

11. A liquid developer composition according to any of claims 1 to 7, wherein the charge-control substance is a metallic salt of an organic acid with an aliphatic chain having at least 6 carbon atoms.

12. A liquid developer composition according to claim 9, wherein as charge-control substance is present a bivalent or trivalent metal salt of
(a) a monoester of diester of an oxyacid derived from phosphorus,
(b) an oxyacid derived from phosphorus and containing one or two organic groups linked to the phosphorus atom by a carbon atom, or
(c) an oxyacid derived from phosphorus and containing an ester group and an organic group linked by a carbon atom to the phosphorus atom, the said organic group being aliphatic, cycloaliphatic or aromatic.

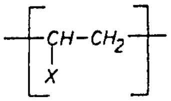
13. A liquid developer composition according to any of claims 1 to 9, wherein as charge-control substance is present a metal alkyl sulphonate, in which the metal ion is a bivalent metal ion which is zinc(II), lead(II), cadmium(II) or copper(II), or is a trivalent metal ion of the group VIII of the Periodic Table of the Elements, and in which the sulphonate group is present directly on an alkyl chain containing at least 6 carbon atoms in a straight line.

14. A liquid developer composition according to any of the claims 1 to 13 and substantially as described herein.

15. A liquid developer composition according to claim 1 and substantially as described in the Examples herein.

16. A method of forming a liquid developer composition suitable for use in developing electrostatic charge patterns and comprising charged toner suspended in an electrically insulating carrier liquid, which method comprises introducing in said liquid comprising a particulate colouring substance, a copolymer (I) and copolymer (II)
said copolymer (I) being a copolymer consisting of 50 to 90 mole% of recurring units of the following formula (A)

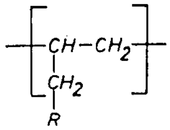
(A)



$$\left[-\underset{X}{CH}-CH_2-\right]$$

wherein X is phenyl or alkylphenyl, and from 10 to 50 mole % of recurring units of the following formula (B)

(B)



$$\left[-\underset{\underset{R}{CH_2}}{CH}-CH_2-\right]$$

wherein R is a hydroxyl group or is a group resulting from the esterification of hydroxyl by means of a C_{12}-C_{20} aliphatic acid with the proviso that the copolymer (I) contains at least 0.5 % by weight of free hydroxyl groups, and said copolymer (II) being:

(a) a copolymer of at least one C_{12}-C_{20} alkyl ester of methacrylic acid (X) and the n-butyl or isobutyl ester of methacrylic acid (Y)

(b) a copolymer of X, Y and up to 70 % by weight of styrene or a vinyl toluene, or

(c) a copolymer of X, Y and up to 0.4 % by weight of methacrylic acid,

the weight ratio of X to Y in this copolymer being between 15:85 and 50:50, the amount of copolymer (I) introduced in said liquid with respect to the colouring substance being in a weight ratio range of 1:1 to 9:1 and the amount of copolymer (II) introduced in said liquid with respect to the colouring substance being in a weight ratio range of 0.5:1 to 5:1.

17. A method according to claim 16, wherein the particulate colouring substance is precoated with copolymer (I) and thereupon copolymer (II) is added to said liquid in the presence of the charge-control substance(s).

18. A method of rendering visible an electrostatic charge pattern on a dielectric material, which method comprises bringing in contact said surface with a liquid developer composition according to any of the claims 1 to 15.

19. A method according to claim 18, wherein said method contains the additional steps of transferring the colouring substance that has been deposited image-wise onto said dielectric material to a receptor material and of fixing said substance thereon.

20. A method according to claim 19, wherein said receptor material is an aluminium sheet that after fixing thereon the image-wise transferred substance is used for planographic printing.

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