PATENT SPECIFICATION (11) 1 571 401

1 571 401

(21) Application No's. 3805/76 (22) Filed 30 Jan. 1976
38023/76 16 Sep. 1975

(62) Divided Out of No. 1571787

(23) Complete Specification Filed 14 Sep. 1976

(44) Complete Specification Published 16 Jul. 1980

(51) INT.CL.[3] G03G 9/12

(52) Index at Acceptance
G2C 1102 1107 1113 1118 1121 1122
1126 1128 1129 1131 1132 C17P

(72) Inventors: NOEL JOZEF DE VOLDER
YVAN KAREL GILLIAMS

(54) IMPROVEMENTS RELATING TO ELECTROPHORETIC DEVELOPER

(71) We, AGFA-GEVAERT, a naamloze vennootschap organized 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 electrostatography and more particularly to a method for the development of positively charged electrostatic charge patterns in the direct sense and negatively charged electrostatic charge patterns in the reverse sense and to liquid developers used therefor.

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 repulsed 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, presently known as cascade, fur brush, powder cloud, magnetic brush and liquid electrophoretic development were introduced.

Developers of the electrophoretic type initially comprised basically 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 has a dielectric constant 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 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, the amount of which can be regulated simply by changing the additive concentration. The polarity is controlled by the appropriate choice of ionogenic substance. For example, a suspension of carbon black in liquid isoparaffins becomes positively charged by calcium diisopropylsalicylate and by the organic phosphorus compounds described in the United Kingdom Patent 1,151,141.

The use of negatively charged toner particle dispersions in which as control agent overbased metal alkyl sulphonates (oil-soluble micells of metal alkyl sulphonates with excess metal hydroxide or carbonate solubilized) are used, has been described in Proc. IEEE, Vol. 60, No. 4, April 1972, page 363 and published German Patent Application

(Dt-OS) 1,966,674.

Examples of said metal alkylsulphonates mentioned in the latter Patent Application are basic alkaline earth metal alkylsulphonates such as $R\text{-}SO_3Ba\text{-}O\text{-}CO\text{-}O\text{-}Ba\text{-}SO_3\text{-}R$ wherein R can be a mixture of various alkyl groups.

According to a further embodiment of said Patent Application a toner dispersion contains a substance which by the formation of a special adsorption phase enhances the dissociative adsorption of the ionogenic compound and allows the control of said adsorption over a wider range. Said substance consists of a soluble, non-ionogenic macromolecular compound whose molecules contain side-chains of at least 4 carbon atoms. As particularly suitable polymers are mentioned substances with side-chains of 10 to 20 carbon atoms. For use in suspensions containing isoparaffines are explicitly mentioned : polymethacrylic acid esters with a molecular weight of 10^4-10^7, polyacrylic acid esters, polyalkylstyrenes, polyvinyl alkyl ethers and copolymers of polymethacrylates with cyclic amides and with fumarates.

A toner developer with toner particles having a negative polarity can be used for direct development of a pattern of positive electrostatic charges or for reversal development of a pattern of negative electrostatic charges such as a pattern resulting from the irradiation of a negatively charged photo-conductor surface. In the latter case the toner is repulsed from the image areas holding negative charges and deposits in the irradiated areas to an extent depending on the charge level differences existing on the surface, in other words, the amount of such negative toner material deposited per increment of surface area is inversely proportional to the magnitude of the negative surface charges retained on the surface.

When attempting to form high density images on a background free of any toner deposit by reversal development of a negative charge pattern using a negative liquid developer, some toner material settles on negative charge-bearing areas, or detects minute charge level differences existing on the irradiated surface, resulting in an undesirable background staining and an overall reduction of contrast, and/or objectionable density variations in the toner image. Minute charge level differences that do not properly belong to the image to be developed are known to occur in particular when using zinc oxide containing layers and they can be caused by uneven charging, incorrect exposure, areas of surface breakdown and the like. Particularly in the reproduction of microfilm containing a negative image of an original positive light-image by projecting that negative image onto a negatively charged photoconductive layer, e.g. containing photoconductive zinc oxide, and reversal developing the electrostatic image by means of a negatively charged toner thereby to obtain a positive reproduction of the original positive light-image, it has proved difficult to obtain a high density developed line image completely free of toner deposit in the image background areas.

The results obtained when using a liquid developer composition for developing a given electrostatic charge pattern depend inter alia on the charge level of the toner. For example in reversal development of a negative electrostatic charge pattern by means of a negative developer, an increase in the charge level on the toner will tend to reduce any tendency for toner to deposit on the charged areas.

The present invention provides liquid developer compositions incorporating a combination of substances serving as dispersing aid and charge control agent, which has been found to enable very useful developer properties to be achieved and in particular a high toner charge level in relation to the amount of control agent employed.

A developer in accordance with the present invention contains a hydrocarbon liquid having a volume resistivity of at least 10^9 Ohm.cm and a dielectric constant of less than 3, a suspended negatively charged toner comprising pigment particles, e.g. carbon black particles, bearing organic polymeric material on their surfaces and at least one organic ionic surfactant, wherein said organic ionic surfactant is an oil-soluble hydrocarbon sulphonate (e.g. an alkyl aryl sulphonate) of magnesium, calcium or barium, the sulphonate having an average molecular weight of at least 800 and a total base number, (as herein defined) of at least 2, and wherein the polymeric material is a copolymer of (A) a C_{12}-C_{20} alkyl alcohol ester of methacrylic acid and (B) n-butyl or isobutyl alcohol ester of methacrylic acid in which the ratio by weight of (A)/(B) is in the range of 15 to 85 to 85 to 15, or is a copolymer which in addition to said monomers A and B in the said weight ratio range contains styrene or styrene homologue units e.g. vinyl toluene units, up to maximum 70% by weight of the total copolymer (said copolymer in either case optionally containing up to 0.4% by weight of methacrylic acid units).

The expression "total base number" (TNB) as used in this specification denotes the quantity of acid, expressed in terms of the equivalent number of milligrams of potassium hydroxide, that is required to neutralize a 1 g sample of the surfactant. This meaning corresponds with that which is attributed to the same expression in ASTM D 664-58 relating to the determination of basic constituents of petroleum products.

Alkaline earth metal hydrocarbon sulphonates for use in a developer according to the present invention as above defined, which sulphonates are referred to hereafter as "overbased" sulphonates, may be prepared according to United States Patent Specification 3,707,360 and are described for use as corrosion-inhibitors in Ind. Eng. Chem. *46*, 5 (1954) p.1035 and 1042.

Developer compositions in accordance with the present invention can be used with advantage for developing electrostatic images comprising image-wise distributed positive charges. At present however the developer compositions are considered to afford greater advantages when used for the reversal development of patterns of negative electrostatic charges. In the latter case the favourable relationship which can be obtained in the developer composition between the amount of charge control agent and the level of charges on the toner can be utilized for developing the negative charge pattern with little or no background staining.

By way of example a very advantageous development method for reversal development of a negative electrostatic charge pattern comprises carrying out such development by means of a developer composition according to the present invention and wherein the toner material is capable of depositing onto negatively charged areas only if their charge level does not exceed a level corresponding with a voltage different from ground of 5 V for a capacitance of about 2×10^{-10} F (farad).cm^{-2}. The amount of charge control agent can be selected to give this result in any given case.

A suitable amount of the sulphonate for a given toner developer can easily be determined by simple tests. By using said 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 0.1 μm to 2μm.

Preferred overbased alkaline earth metal hydrocarbon sulphonates are listed in the following Table 1.

TABLE 1

Compound no.	Trade name	% by weight metal ion	TBN mg KOH/g	Average molecular weight of the sulphonate
1	TLA-414	Ca^{++} 16.2%	400	>900
2	TLA-107	Ba^{++} 14.2%	35	>900
3	SINTSUL Mg	Mg^{++} 8-9%	310	920-970
4	TLA-256	Ca^{++} 2.1%	10	800-900

TLA-414 is the trade name of a highly overbased calcium hydrocarbon sulphonate marketed by TEXACO Inc., Petro Chemical Dept., 135 East 42nd Street, NEW York, N.Y. 10017.

TLA-107 is a slightly overbased calcium hydrocarbon sulphonate marketed by the same company.

SINTSUL Mg is the trade mark for a highly overbased magnesium hydrocarbon sulphonate marketed by LIQUICHIMICA s.p.a. Milano, Italia.

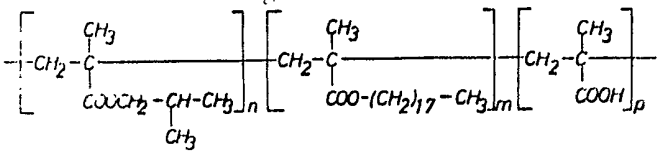
Preferred copolymers for use according to the present invention have a molecular weight of at least 40,000. Examples of preferred copolymers are listed in Table 2.

TABLE 2

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

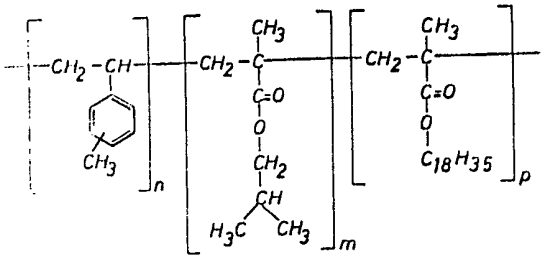
NEOCRYL B702 is a trade mark of Polyvinyl Chemie - Holland, Waalwijk, Netherlands for a copolymer of isobutyl methacrylate, stearyl methacrylate and methacrylic acid.

NEOCRYL B702 has the following structure:



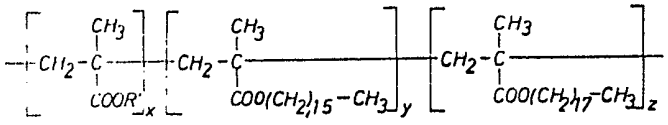
wherein :
n = from 75 to 85% by weight
m = 15 to 25% by weight
p = about 0.2% by weight

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:



wherein:
R' = n-butyl
x = 56% by weight
y = 26% by weight
z = 18% by weight

The insulating liquid used as a carrier fluid may be any of the conventional electrically insulating carrier liquids generally employed in liquid developer compositions. Said liquid may be 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 an aliphatic hydrocarbon preferably having a boiling range between 150°C and 220°C such as ISOPARS G, H, K or L (trade marks) of Exxon and SHELLSOL T (trade mark) of Shell Oil Company.

The colouring agent used in the toner particles may be of any of the pigments and solid dyestuffs 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 and SPEZIAL SCHWARZ IV (trade names of DEGUSSA - Frankfurt/M, W. Germany).

Very suitable carbon black pigments are marketed by DEGUSSA under the trade mark PRINTEX. PRINTEX 140 and PRINTEX G are representatives thereof. The characteristics of preferred carbon blacks are listed in the following Table 3.

TABLE 3

	SPEZIAL SCHWARZ IV	PRINTEX 140	PRINTEX G
origin	oxidized channel black	channel black	furnace black
density	1.8 $g.cm^{-3}$	1.8 $g.cm^{-3}$	1.8 $g.cm^{-3}$
grain size before entering the developer	25 nm	29 nm	51 nm
oil number (g of linseed oil adsorbed by 100 g of pigment)	300	360	250
specific surface (sq.m per g)	180	96	31
volatile material % by weight	14	6	2
pH	3	5	8
colour	brown-black	brown-black	bleu-black

As colour corrector for the carbon black pigments preferably minor amounts of copper phthalocyanine are used, e.g. from 1 to 20 parts by weight with respect to the carbon black.

The organic polymeric material on the pigment particles operates as a dispersing aid and agent controlling the adsorption of the charge determining ionic species of the ionogenic surfactant. In addition the coating of the described polymeric material confers on the toner developers a better shelf life stability.

The organic polymers may be used in amounts of between 10% to 500% by weight with respect to the total weight of pigment particles, preferably between 20% and 200% by weight.

The polymeric material is preferably introduced as a separate ingredient in the developer liquid and allowed to become adsorbed onto the pigment particles.

It is generally suitable for the electrophoretic liquid developer to incorporate the toner in an amount between 0.1 g and 20 g per litre of liquid. The said amount preferably between 0.5 g and 10 g per litre.

The alkaline earth metal hydrocarbon sulphonates are preferably used in the range of 1 to 250% by weight with respect to the pigment particles, more preferably in a range of 10 to 100% by weight.

The liquid developer composition 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. a 3-roll mill, ball mill, colloid mills, high speed stirrers, a concentrate e.g. 15 to 80% by weight of solids in the insulating carrier liquid of the materials selected for the composition and subsequently to add further insulating carrier liquid to provide the liquid developer composition ready for use in the electrostatic reproduction process.

The electrophoretic development may be carried out 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, e.g., in certain medical X-ray images for diagnostic purposes.

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

Example 1

In a ball-mill the following products were introduced successively :

- 50 ml of 10% solution of TLA-414 (trade name) (total base number : 400) in isododecane
- 2 g of PRINTEX G (trade name).

This mixture was ground for 15 h and thereupon diluted with isododecane so as to obtain a toner dispersion having 0.4 g per litre of carbon black with mean grain size of 0.36 µm. By tests carried out in an electrophoresis cell it could be determined that actually only 75% of the toner particles had a negative charge. To said toner dispersion 1.5 g of NEOCRYL B 702 (trade name) were added. After an additional 2 hours of ball-milling 10 ml of dispersion were diluted with 1 litre of isododecane so as to obtain the working developer. The mean diameter of the toner particles was now 0.31 µm. By tests carried out in an electrophoresis cell it could be determined that all particles were negatively charged.

Said developer was used for reversal development of a negatively charged image obtained on a photoconductive zinc oxide coating by exposure through a negative microfilm half-tone image.

The photoconductive layer was initially charged up to a charge level of 300 V for a capacitance of about 2×10^{-10} F.cm^{-2}. In the exposed portions the charge level was dropped to about 5 V. A clear image background was obtained.

The visible image obtained had only slight graininess, a good uniformity and an optical density equal to 1.0 (measured by reflected light).

The storage keepability of the above prepared developer was more than 5 months.

Example 2

In a ball-mill the following ingredients were introduced successively :

NEOCRYL B 702 (trade name)	1.0 g
PRINTEX G (trade name)	4.0 g
TLA-414 (trade name)	0.04 g
isododecane	46 ml

After 15 h of ball-milling 10 ml of dispersion were diluted with 1 litre of isododecane. The average diameter of the negatively charged toner particles was 0.42 µm.

The obtained developer is particularly useful in electrophoretic development to produce toner images that can be transferred from a smooth surface e.g. resin surface to plain paper.

Example 3

In a ball-mill the following ingredients were introduced successively:

NEOCRYL B 702 (trade name)	1.5 g
PRINTEX G (trade name)	2 g
TLA-256 (trade name)	0.5 g
isododecane	47 ml

After 15 h of ball-milling 10 ml of the obtained toner concentrate were diluted with 1 litre of isododecane. The average diameter of the negatively charged toner particles was 0.50 µm.

Example 4

In a ball-mill the following ingredients were introduced successively:

PLEXOL 618 (trade name)	10 g
PRINTEX G (trade name)	2 g
TLA-414 (trade name)	0.4 g
isododecane	39 ml

After 15 h of ball-milling 10 ml of the obtained toner concentrate was diluted with 1 litre of isododecane.

The negatively charged toner is suited for reversal development and is self-fixing.

Example 5

In a ball-mill the following ingredients were introduced successively :

NEOCRYL B 707 (trade name)	1.5 g
PRINTEX G (trade name)	2 g
TLA-414 (trade name)	0.4 g
isododecane	46 ml

The average diameter of the negatively charged toner particles was 0.27 μm. The toner adhered perfectly to photo-conductive zinc oxide coatings.

Example 6

In a ball-mill the following ingredients were introduced successively :

NEOCRYL B 702 (trade name)	1.5 g
SPEZIAL SCHWARZ IV (trade name)	2 g
TLA-414 (trade name)	0.4 g
isododecane	47 ml

A toner dispersion of very good stability containing toner particles having an average diameter of 0.25 μm was obtained.

WHAT WE CLAIM IS:-

1. A liquid developer composition suitable for rendering visible in the direct or reversed sense electrostatic charge patterns contained on a surface, which composition contains in a hydrocarbon liquid having a volume resistivity of at least 10^9 Ohm.cm and a dielectric constant of less than 3, a negatively charged suspended toner comprising pigment particles bearing organic polymeric material on their surfaces and at least one organic ionic surfactant, wherein

(1) said organic ionic surfactant is an oil-soluble hydrocarbon sulphonate of magnesium, calcium or barium, the sulphonate has an average molecular weight of at least 800, and a total base number, (as herein defined) of at least 2, and

(2) the polymeric material is a copolymer of (A) a C_{12}-C_{20} alkyl alcohol ester of methacrylic acid and (B) n-butyl or isobutyl alcohol ester of methacrylic acid in which the ratio by weight of (A)/(B) is in the range of 15 to 85/85 to 15 or is a copolymer which in addition to said monomers A and B in the said weight ratio range contains styrene or styrene homologue units up to maximum 70% by weight of the total copolymer (said copolymer in either case optionally containing up to 0.4% by weight of methacrylic acid units).

2. A liquid developer composition according to claim 1, wherein as earth alkali metal hydrocarbon sulphonate a compound of Table 1 is present.

3. A liquid developer composition according to claim 1 or 2, wherein as polymeric material a copolymer of Table 2 is present.

4. A liquid developer composition according to any of the preceding claims, wherein the pigment particles are carbon black particles.

5. A liquid developer composition according to claim 4, wherein the carbon black particles are mixed with copper phthalocyanine particles to obtain a more neutral black colour tone of deposited toner.

6. A liquid developer composition according to any of the preceding claims, wherein the insulating carrier liquid is an aliphatic hydrocarbon.

7. A liquid developer composition according to claim 6, wherein said carrier liquid is isododecane.

8. A liquid developer composition according to any of the preceding claims, wherein the negatively charged toner particles have a size in the range of 0.1 to 2 μm.

9. A liquid developer composition according to any of the preceding claims, wherein the alkaline earth metal hydrocarbon sulphonate is present in an amount of from 1.0 to 250% by weight with respect to the total weight of the pigment particles.

10. A liquid developer composition according to any of the preceding claims, wherein the copolymer is present in an amount of between 10% to 500% by weight of pigment particles.

11. A liquid developer composition according to any of the preceding claims, wherein the toner particles are present in an amount between 0.1 g and 20 g per litre of liquid.

12. A method of forming a liquid deveoper having a composition according to any of

claims 1 to 11, which method comprises dispersing the pigment particles in said liquid in the presence of said organic polymeric material and said ionic surfactant.

13. A method of reversal developing a negative electrostatic charge pattern comprising negative electrostatic charges on a surface, which method comprises contacting said surface with a liquid developer composition according to any of claims 1 to 11.

14. A method according to claim 13, wherein the charges on the toner material are of such magnitude that such material is repelled by negatively charged areas of said surface unless the surface charge level does not exceed a level corresponding with a voltage difference from ground of 5 V for a capacitance of about 2×10^{-10} F.cm^{-2}.

HYDE, HEIDE & O'DONNELL,
Chartered Patent Agents,
47 Victoria Street,
London SW1H 0ES.
Agents for the Applicant.

Printed for Her Majesty's Stationery Office, by Croydon Printing Company Limited, Croydon, Surrey, 1980.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY,from which copies may be obtained.