LIQUID DEVELOPER WITH SHARP CUT-OFF RESPONSE

Filed March 2, 1965

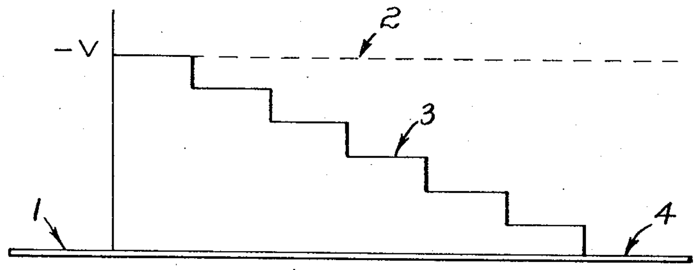

FIG 1

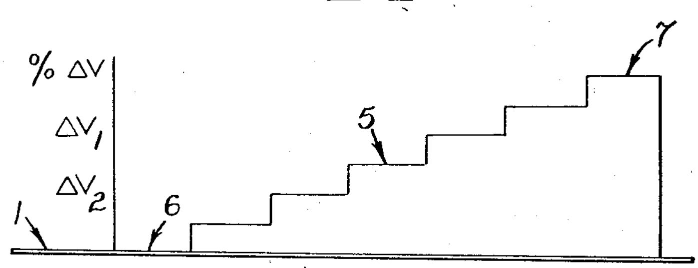

FIG 2

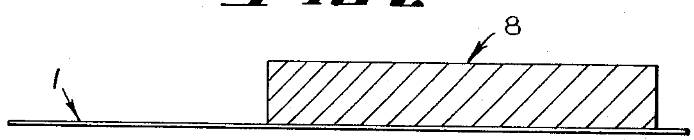

FIG 3

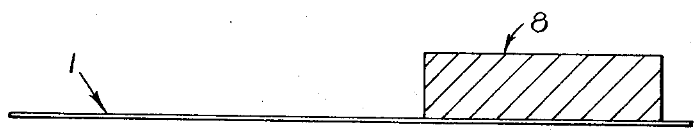

FIG 4

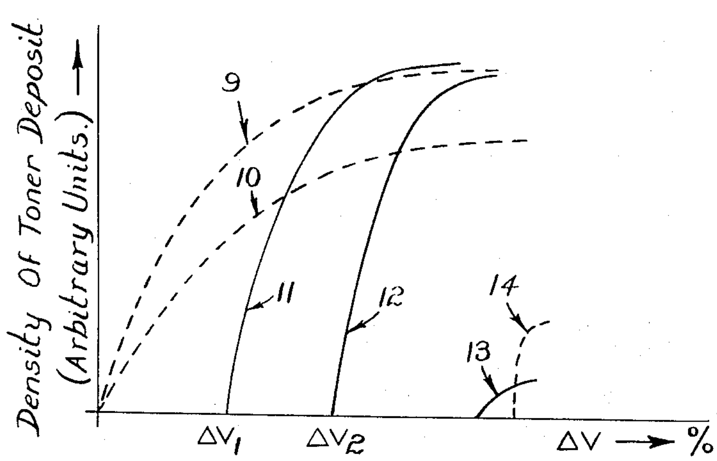

FIG 5

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LIQUID DEVELOPER WITH SHARP CUT-OFF RESPONSE

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4 Claims. (Cl. 252—62.1)

ABSTRACT OF THE DISCLOSURE

Superior response for image development in electrostatic printing, using liquid developers, is achieved by dissolving in the carrier liquid an oil, such as a mineral oil, itself containing additions, inclusive of an oxidation inhibitor and a detergent-dispersant.

This invention relates to electrophotography and more particularly to improved methods of and means for rendering visible in the reverse sense latent images formed by negative electrostatic charges on electrophotographic and on insulating surfaces such as are known in electrostatic printing.

In one type of electrophotography a relatively conductive backing member such as metal or paper sheet having deposited thereon a photoconductive material such as for instance vitreous selenium or an organic photoconductor or a particulate photoconductor such as zinc oxide in a resin binder commonly known as an electrophotographic or Electrofax layer is first subjected to a corona discharge whereby a uniform electrostatic charge is deposited on to the surface of the photoconductive layer. The charged surface is then exposed to a radiation pattern whereby the irradiated areas become discharged in accordance with the intensity of radiation whereas the shielded areas remain charged and thus form a latent electrostatic image. Such latent image is then rendered visible by applying thereto a dry powder developer or toner material suspended in an insulating carrier liquid in order that such toner may be attracted and held electrostatically to the charged areas. The thus developed image may be fixed to the surface of the photoconductor or transferred to another surface and fixed thereon.

In the liquid developing process it is customary to prepare a liquid developer by suspending a particulate pigment wetted with an oil or resin in an insulating carrier liquid to the form the toner material to be deposited electrostatically. The polarity of the toner material with respect to the latent image to be developed is determined by the nature of the materials selected or by so-called polarity control agents as described for instance in U.S. Patents No. 2,907,674 of K. A. Metcalfe et al., and 3,076,722 of H. G. Greig.

In the prior art it is known to produce so-called positive and negative liquid developers. A positive developer contains toner material which can be attracted by negative charges and therefore it can be used for instance to develop a latent image formed by negative electrostatic charges on a charged and exposed zinc oxide coated electrophotographic paper, the resulting image being a facsimile reproduction of the original radiation pattern. A negative developer contains toner material which can be attracted by positive charges or repelled by negative charges. Electrophotographic coatings containing zinc oxide can be charged only negatively with the result that the latent image formed by exposure is negative in polarity. The negative developer can be applied to a zinc oxide layer containing a negative latent image to produce a reversal reproduction of the original radiation pattern by toner repulsion from the image areas holding negative charges and by deposition on to the exposed areas in accordance with the charge level differences existing on the surface that is to say the rate of deposition of such negative toner material is inversely proportional to the magnitude of the negative surface charges retained on the surface.

One of the problems in producing in the reverse sense high density images on a background free of any toner deposit employing negative liquid developers is that the toner material is sensitive enough to detect even minute residual charges or charge level differences existing on the exposed surface and consequently such minute charges or charge level differences result in deposition of toner material according to their intensity and thus give rise to the formation of undesirable background staining and an overall reduction in contrast. Such minute charges and charge level differences are known to exist in particular on zinc oxide containing layers and they can be caused by uneven charging, inadequate exposure, areas of surface breakdown, coating artifacts and the like. Particularly in the process of microfilm reproduction or in any other process where a negative light image is projected on to a zinc oxide containing electrophotographic sheet for the purpose of obtaining a reversal that is a positive reproduction of the original light image by developing with a negative toner, it has not been possible in the prior art processes to obtain a high density line image for instance of printed matter on a background completely free of toner deposit because in projection exposure it is unavoidable that the background areas on the surface of the photoconductor become exposed to some degree of illumination and this is particularly the case with low density negatives wherein the background areas are not fully opaque and the image areas are not fully transparent. Such exposure of the background areas results then in charge reduction and in charge level differences with consequent toner deposition on to such background areas forming undesired contamination and an overall loss in contrast.

An object of the present invention is to provide a liquid developer for developing in the reverse sense latent images formed on a surface by negative electrostatic charges which developer contains negative toner material capable of depositing only on to such areas where the maximum magnitude of the original negative charges contained on the surface has been reduced by exposure by at least a predetermined percentage.

A further object is to provide an electrostatic liquid developer which is capable of forming high density image deposits without developing undesired charge reductions caused by processing defects.

A still further object is to provide an electrostatic liquid developer which is capable of producing high contrast positive reproductions from low density negatives.

The foregoing objects and other advantages will be apparent from the following detailed description of this invention.

A developer in accordance with this invention consists of an insulating carrier liquid having an electrical volume resistivity in excess of 10^9 ohm cm. and a dielectric constant of less than 3, toner particles of limited sensitivity suspended in said carrier liquid which particles may comprise pigment particles or aggregates of pigment particles containing thereon an adsorbed layer of a wetting substance and a sensitizing agent dissolved in said carrier liquid capable of affecting the sensitivity of said toner particles without being capable of depositing electrostatically.

The above referred to toner particles are termed to be of limited sensitivity in that when suspended in the desired carrier liquid in absence of the sensitizing agent they are of insufficient sensitivity to develop to any appreciable density the unexposed areas containing a residual negative charge or the exposed areas when acting as negative toners.

In order that the functioning of the liquid developer in accordance with this invention may be fully understood it is necessary to first describe the mechanism of developing a latent image. On a surface containing latent images formed by negative electrostatic charges of varying magnitude there is a flux of a density varying in proportion to the magnitude of the said negative charges. This flux can be imagined as issuing from the negative latent image areas in a density proportional to the surface charge magnitude in such areas and re-entering the surface in the exposed non-image areas containing lesser or no residual negative charges. The density of this re-entrant flux in any area is inversely proportional to the magnitude of the residual negative charges present in the area. Positive toner particles deposit along the field lines towards the negative charge and their rate of deposition is proportional to the magnitude of the negative charges or to the density of the flux issuing from the charge holding areas whereas negative toner particles deposit along the field lines towards the point of re-entry and their rate of deposition is inversely proportional to the magnitude of the residual negative electrostatic charges existing in the exposed or partly exposed areas.

It will be thus seen that prior art negative toner particles will not deposit on to the unexposed areas retaining negative charges of the maximum magnitude characteristic of a given surface but toner deposition will take place on to all other areas where the charge magnitude has been reduced by exposure or due to other causes to a magnitude lesser than the aforesaid maximum. The rate of deposition of the negative toner that is to say the image deposit in a given area is therefore proportional to the exposure or to the percentage of reduction of the aforesaid maximum charge magnitude that is to say to the difference between the aforesaid maximum charge magnitude in the unexposed areas, where no toner deposition takes place, and the lesser charge magnitude existing in the given area. The highest density image deposit can be thus attained in fully exposed areas approaching 100% reduction of the aforesaid maximum charge magnitude retained in the unexposed areas.

In view of the foregoing it is apparent that there is need for a negative liquid developer as provided by this invention for the production of reversed or positive copies from negatives which developer contains toner material which is not capable of depositing on to areas where the maximum magnitude of the original surface charge contained on the surface has not been reduced by at least a predetermined percentage in order to prevent rendering visible the aforesaid effects due to partial illumination of the non-image areas of the photoconductive surface in case of projection exposure from low density negatives, due to uneven charging, artifacts and the like.

To further explain the functioning of the liquid developer in accordance with this invention reference is made to the accompanying drawings in which:

FIGS. 1 and 2 show residual surface charges and corresponding charge differences that is percentages of charge reduction on the surface of an exposed electrophotographic layer,

FIGS. 3 and 4 show toner deposition in accordance with this invention on to the surfaces shown in FIGS. 1 and 2, and

FIG. 5 is a diagram showing curves of toner characteristics in accordance with the prior art and in accordance with this invention.

Referring now to FIG. 1, an electrophotographic printing element such as a zinc oxide coated paper is shown here the surface **1** of which has been charged to a negative potential of magnitude **2** and subsequently exposed to a light pattern of varying intensity whereby the initial charge **2** has been reduced to various steps **3** extending to a fully exposed area **4** with complete charge removal. Positive toner material as known in the prior art would deposit in proportion to the charge levels $-V$.

In FIG. 2 the various charge levels of FIG. 1 are shown as charge level differences that is charge reduction percentages in relation to the initial highest charge **2** of FIG. 1. It will be noted that the highest percentage of charge reduction **7** is in the portion corresponding to the fully exposed area **4** of FIG. 1, no charge reduction exists in portion **6** corresponding to the area of FIG. 1 where the initial charge **2** has been fully retained due to no illumination and intermediate step **5** corresponds to the partially exposed step **3** of FIG. 1. Toner deposition from a negative liquid developer as shown in the prior art would be proportional to the percentage of charge reduction DV.

In FIG. 3 is shown toner deposition according to the charge reductions of FIG. 2 using a negative liquid developer in accordance with this invention. It will be noted that there is a response cut-off at the charge reduction percentage DV_2 of FIG. 2, in that no toner deposition takes place on to areas where the charge reduction is below this critical percentage, but toner deposition **8** takes place at a uniform rate in all areas where the charge reduction percentage is equal to or higher than DV_2. Such response cut-off at a desired charge reduction percentage is attainable in accordance with this invention by employing the aforementioned sensitizing agent which agent in a developer system containing toner material of limited sensitivity may sensitize each toner material and may confer to the developer system a response cutoff at any desired charge reduction percentage depending on the quantity and type of such sensitizing agent employed.

In FIG. 4 is shown toner deposition as in FIG. 3 except that here less sensitizing agent was imployed and consequently the sensitivity of the toner material initially of limited sensitivity has been increased to a lesser degree than of that in FIG. 3. As a result the cut-off of the toner in FIG. 4 occurs at a greater percentage of charge reduction DV_1. Toner deposition takes place at a uniform rate and only in areas **8** where the charge reduction is equal to or higher than DV_1.

The functioning of the sensitizing agent can be now explained as follows: As stated previously the liquid developer according to this invention contains toner particles of limited sensitivity suspended in a carrier liquid and such toner particles can be of either polarity initially irrespective of their required final negative polarity because their sensitivity is so limited that their capability of depositing in absence of the sensitizing agent is negligible. The sensitizing agent is a substance which is completely soluble in the carrier liquid in the form of macromolecules or molecular chains or micelles. When dissolved in the carrier liquid each macromolecule or micelle carries a small positive charge sufficient in magnitude to create an environment of positive polarity around the toner particles in suspension but not sufficient in magnitude to be attracted by and deposited on to the negatively charged areas on the image bearing surface. The toner particles in the positive environment created by the sensitizing agent assume a negative polarity relative thereto and are thus urged by the sensitizing agent to deposit as apparently negatively charged particles on to the image bearing surface in areas where the negative surface charge has been reduced by at least a certain percentage.

The magnitude of the apparent negative charge acquired by the toner particles depends on a particular system on the type of the sensitizing agent and is proportional to the concentration thereof in relation to the toner particle concentration. Consequently, the capability of the thus sensitized toner particles to deposit is proportional to their aforesaid magnitude of apparent negative charge acquired relative to the sensitizing agent and this magnitude of charge determines the percentage of negative charge reduction required on the surface below which no toner deposition will take place that is to say where the cut-off occurs.

The proportioning of the sensitizing agent for obtaining a particular cut-off may vary from system to system depending on the mobility of the toner particles in the carrier liquid and on the type of sensitizing agent used. As will be shown in the examples following this disclosure one type of sensitizing agent may be more effective than another type in a given developer system. In each case however the quantity of the sensitizing agent present in the system is relatively small because a very small quantity of the agent is already sufficient to create a positive environment around the toner particles and variations of this small quantity can be made to adjust the toner sensitivity to the required cut-off. In any case the quantity of the sensitizing agent employed must be insufficient to lower the volume resistivity of the carrier liquid in order that the electrostatic image contained on the surface to be developed may not be destroyed.

The sensitizing agent must not have the tendency to adsorb preferentially on to the toner particles containing the absorbed layer of the wetting substance because a toner particle having the sensitizing agent adsorbed thereon to any substantial degree would assume the positive polarity thereof and thus function as a positive developer which is contrary to the provisions of this invention.

The sensitizing agent can be incorporated either by first dissolving it in the carrier liquid and then suspending the toner particles in the solution or by dissolving it in the carrier liquid containing the toner particles in suspension or by mixing it with toner material comprising pigment particles milled with a wetting substance and then suspending such mixture in the carrier liquid.

We found that numerous substances such as vegetable oils, mineral oils, mineral greases, metallic soaps, varnishes, resins, waxes and bitumenous compounds provided that they are fully soluble in the desired carrier liquid in the form of macromolecules or micelles or molecular chains creating a positive environment around the toner particles can be used as sensitizing agents. In particular we found that mineral oils such as used in automotive lubrication, engine lubrication, internal combustion engines, hydraulic equipment and the like can be used with advantage as sensitizing agents, the most effective of such being the mineral oils containing both the customary oxidation inhibiting and detergent-dispersant additives. As will be seen in the examples the percentage of such additives in the mineral oil is related to the degree of effectiveness of the oil as sensitizing agent. We also found that the mineral oil as the carrier of the said additives is per se essential in the sensitizing agent in that when dissolved in the carrier liquid in the form of macromolecules of molecular chains or micelles each of such having attached thereto the polar/non-polar molecules of the additives, it effects an even distribution in the carrier liquid of such molecular chains or micelles forming the positive environment around the suspended toner particles.

Whilst not being bound to any theory it can be explained that the positive environment created in the aforesaid manner is due to the orientation of the polar/non-polar molecules of the additives attached to the macromolecules or molecular chains or micelles of the mineral oil dissolved in the carrier liquid of high volume resistivity.

The dependence of the toner sensitivity on the sensitizing agent can be further explained with reference to FIG. 5. Curves **9** and **10** represent the density of images obtained by deposition of prior art negative toners, and it will be noted that the density is proportional to the percentage of charge reduction, curve **9** representing a toner with higher rate of deposition than the toner represented by curve **10**. Curves **13** and **14** represent the density obtained by deposition from the liquid developer in accordance with this invention comprising a liquid carrier with suspended toner particles of limited sensitivity in absence of the sensitizing agent. Deposition of toner represented by curve **13** commences only at a very high percentage of charge reduction and the density is negligible. The density of deposition of toner represented by curve **14** is somewhat higher but this toner is even less sensitive than the toner of curve **13**. Curve **12** represents the characteristics of a developer prepared by adding a proportion of the sensitizing agent to the toner suspension of curve **13**. It will be noted that the sensitivity of the toner of curve **12** has been increased over that of curve **13** in that deposition takes place at a much lower percentage of charge reduction, and the density of deposit is now high. Upon further addition of sensitizing agent the toner of curve **11** was obtained, and it will be noted that the sensitivity has been further increased. Points DV_1 and DV_2 on curves **11** and **12**, respectively, correspond to the cut-off points in FIGS. 2, 3 and 4. It will be noted that the density of toner deposit according to curves **11** and **12** is not proportional to DV to the extent as that of curves **9** and **10** in that deposition of toner represented by curves **11** and **12** is relatively uniform for all values of DV above the cut-off point that is above the critical minimum percentage of charge reduction.

Such uniform toner deposition in accordance with this invention is also shown in FIGS. 3 and 4, and it can be explained by the nature of these developers wherein the toner particles having been sensitized by the sensitizing agent only to a restricted extent in order to avoid deposition below a certain percentage of charge reduction, the force of attraction caused by the field in the relevant areas has been also restricted to such extent that irrespective of the magnitude of the charge reduction above the critical value, only a toner deposit of a certain thickness can be held in position and further toner particles which move to areas where the charges have been further reduced can not be held in position at such areas due to the aforementioned restricted force of attraction, particularly in view of their relatively greater distance from the surface than that of the toner particles already deposited.

We found that on commercially available zinc oxide containing electrophotographic papers employed in this process of reversal reproduction by means of liquid developers provided by this invention it is necessary to sensitize the toner particles in such manner that they will not deposit on to areas where the initial negative charge has not been reduced by at least 70% in order to prevent the visual reproduction of processing defects, whereas in projection reproduction from low density or low contrast microfilm negatives we found that high contrast copies can be obtained if the toner particles are sensitized so that no deposition will take place on to areas where the initial negative charge has not been reduced by about 85%.

In preparing a liquid developer in accordance with this invention by one method pigment particles of high sensitivity for a surface charge of one polarity are rendered of limited sensitivity by adsorbing on to them a wetting substance of high sensitivity for a surface charge of opposite polarity in such quantity that the resulting response of the thus coated particle to a negative or positive surface charge becomes limited to the desired degree. By another method the toner particles comprise two or more types of pigments wherein each pigment particle contains an adsorbed layer of one or more types of wetting substances or polarity control agents as known in the prior art and wherein such particles are arranged in the form of aggregates in such manner and in such proportion with regard to the sensitivity of the individual types of particles, wetting substances and control agents that the resulting overall sensitivity of the aggregate as a whole to a negative or positive surface charge becomes limited to the desired degree.

The wetting substance referred to in the foregoing, which in method one acts as a dispersing aid only whereas in the second method it may also affect the polarity of the toner particles, can be an oil, a resin, a varnish or wax which can be adsorbed on to the particles by milling or other methods of dispersion and which also facilitates the suspension of the toner particles in the carrier liquid. Such wetting substance can be therefore soluble, partially soluble or insoluble in the carrier liquid but it must remain at least in part as a thin coating on the particles suspended in the carrier liquid to form coated toner particles on which such coating cannot become replaced by the sensitizing agent adsorbing from solution in the carrier liquid on to the particles and therefore the wetting substance can also be incompatible with the sensitizing agent in order to prevent its adsorption on to the particles in a quantity sufficient to confer the polarity characteristics of the sensitizing agent to the coated particles. The proportion in which such wetting substance may be used in relation to the pigment to form the toner particles may be determined by the wetting properties of the particles and by the wetting power of the wetting substance, but in the second method polarity characteristics of both of the particles and of the wetting substances may determine the necessary proportion to attain toner particles of limited sensitivity.

It will be seen from the foregoing that in contrast to the prior art liquid developers wherein the response of toner particles is governed by a coating of a polarity control agent determining the magnitude and polarity of the charge contained on the particle and wherein such control agent contained as a coating on the particle co-deposits therewith on to the photoconductive surface, in the liquid developers in accordance with this invention the agent governing the response of the toner particles with respect to polarity and degree of response or sensitivity is the sensitizing agent which is not present in the form of a coating on the toner particles but is in a dissolved state in the carrier liquid without lowering the volume resistivity thereof and furthermore such sensitizing agent is opposite in polarity to that which it confers to the toner particles and it does not co-deposit with the toner particles on to the areas to be developed nor does it deposit on to the non-image areas.

The following examples of toner formulations will further illustrate the manner in which liquid developers with varying cut-off response can be prepared in accordance with this invention and it will be realised that this invention is not restricted by the cited materials and combinations thereof as one skilled in the art of making electrostatic developers can utilise the teachings of this invention to select and proportion other materials in order to obtain liquid developers with cut-off characteristics as may be desirable for particular applications.

Example 1

In these examples the cut-off characteristics are expressed as percentages of reduction of the negative charges of maximum magnitude retained on the image bearing surface after exposure to electromagnetic radiation, 100% charge reduction relating to fully exposed and discharged areas.

The response cut-off of this developer is at 80% of charge reduction that is to say at least 80% of the maximum magnitude of the negative charge held on the surface in any area is to be removed by exposure before toner deposition can take place.

Toner particles of limited negative sensitivity are prepared here by coating a strongly positive pigment particle with a strongly negative resin as the wetting substance. The toner concentrate is prepared by wetting the pigment.

Irgalite Fast Brilliant Blue GLS—10 grams

with the resin

Pentacite P–423 (30% solution in toluene)—30 grams

by milling or other methods. To the pigment dispersion is then added by stirring

Mobilgrease No. 5—10 grams

as the sensitizing agent. This grease contains about 20% of a sodium stearate soap.

The above toner concentrate can be suspended in the proportion ranging from 0.1 to 10% by weight in a carrier liquid such as for instance Shell X55 solvent, n-heptane, n-hexane, Shellsol T solvent, Shell X4 solvent, trichlorotrifluoroethane and the like. the Mobilgrease No. 5 being fully soluble whereas the Pentacite P–423 being substantially insoluble in these carrier liquids. The toner concentration may depend on the method of developing preferred.

Example 2

The response cut-off of the developer of Example 1 was raised to 90% by decreasing the quantity of the Mobilgrease No. 5 sensitizing agent to 5 grams. In this case the grease was first dissolved in the carrier liquid in the proportion of 1 gram of the grease to 100 grams of the carrier liquid and then 8 grams of the pigment dispersion were suspended in the solution.

Example 3

The response cut-off of this developer is at 90%.

The toner particles are of limited negative sensitivity and consist of coated particle aggregates which are prepared as follows:

	Grams
Microlith Bordeaux RT pigment	20
Microlith Green GT pigment	20
are wetted with the resin	
Superbeckosol 1352	20

by milling or other methods to form a pigment dispersion.

Both the Bordeaux RT and the Green GT pigments contain a coating of Staybelite Ester 10 resin on the particles. The pigments without such coating are negative but the strongly positive resin converts the Bordeaux pigment to a toner of limited positive sensitivity and it also reduces the negativity of the Green pigment. When thus the two coated pigments form an aggregate in the above proportion, the response of such aggregate is of limited negative sensitivity. To obtain adequate dispersion the Superbeckosol resin, which does not affect the response of the coated particles, has been used as a wetting substance which also prevents due to incompatibility adsorption of the sensitizing agent on to the coated particle aggregates.

To the above pigment dispersion is added and mixed by stirring

Ampol automotive oil 20/20W—5 grams

as the sensitizing agent to form the toner concentrate. This mineral oil contains 0.5–1.0% by volume of oxidation inhibiting additives and 1.0–2% of detergent-dispersant additives.

According to the method of developing preferred, the above toner concentrate can be dispersed in the proportion ranging from 0.1–10% by weight in a liquid carrier as disclosed in Eràmple 1 and in addition in Isopar H, mineral spirits, cyclohexane, perchlorethylene and carbon tetrachloride.

Example 4

The response cut-off of the developer of Example 3 was reduced to 70% by increasing the quantity of the sensitizing agent Ampol automotive oil 20/20W in the toner concentrate from 5 grams to 15 grams.

Example 5

The Ampol automotive oil 20/20W of Example 4 was replaced with

Shell X100, SAE 40 rating, automotive oil,

having similar percentages of additives, as the sensitizing agent.

Example 6

The 15 grams of the Ampol 20/20W oil of Example 4 were replaced with 7.5 grams of

Valvoline Super HPO automotive oil,

which mineral oil contains 0.5–1.5% of oxidation inhibiting additives and 3.0–5.0% of detergent-dispersant additives.

The response cut-off was maintained at 70% despite of halving the quantity of the sensitizing agent in view of the higher concentration of the additives therein.

Example 7

The 15 grams of the Ampol 20/20W oil of Example 4 were replaced with 2 grams of

BP Energol HD–S3 Diesel engine oil

which mineral oil contains 0.5–2.0% of oxidation inhibiting additives and 10–20% of detergent-dispersant additives.

The response cut-off was at 75%.

Example 8

Toner particles of limited positive sensitivity are prepared hereby coating a negative pigment with a positive resin in the following manner:

	Grams
Carbon black pigment	10
Staybelite Ester 10 resin (30% solution in toluene)	15

are milled to form the toner particles of limited positive polarity. This dispersion is then further milled with

Bodied linseed oil—10 grams.

to obtain a concentrate wherein the linseed oil forming the final coating on the toner particles whilst not affecting the sensitivity thereof protects the particles from adsorbing the sensitizing agent from the carrier liquid.

This toner concentrate was suspended in the carrier liquids of Example 3 in the proportion of 3.5 grams of toner concentrate to 100 grams of the carrier liquid. In the carrier liquids containing the toner suspension was then dissolved

Paraffin oil as the sensitizing agent

in various proportions up to 10 grams of paraffin oil to 100 grams of the carrier liquid. At this high concentration toner sensitivity with a response cut-off at about 95% was noticed but rate of deposition was inadequate in view of the lowered volume resistivity of the carrier liquid and lessened mobility of particles due to the high oil concentration.

The sensitizing agent was then rendered more effective by the incorporation in

	Grams
Paraffin oil	100
of the oxidation inhibiting additive	
Zinc alkyl dithiophosphate	1
and of the detergent-dispersant additive	
Sodium naphtha sulphonate	4

4 grams of this sensitizing agent were then dissolved in the carrier liquids containing 3.5 grams of the toner concentrate and a developer was obtained with a response cut-off at 80% of charge reduction.

Example 9

The paraffin oil of Example 8 was replaced with the sensitizing agent

Valvoline Crystal lubricating oil,

which is a mixture of paraffinic and naphthenic mineral oils and is free of additives. The response cut-off was at 70% using the same additives in the same proportion as in Example 8.

Example 10

The oxidation inhibiting additive of Example 8 was replaced with

phenyl-b-naphthylamine.

The response cut-off was at 60%.

Example 11

The oxidation inhibiting additive of Example 9 was replaced with

phenyl-b-naphthylamine.

The response cut-off was at 55%.

Example 12

The oxidation inhibiting additive of Example 8 was replaced with

2,6-di-tert-butyl-alpha-dimethylamino-para-cresol.

The response cut-off was at 75%.

Example 13

The detergent-dispersant additive of Example 8 was replaced with

Sodium alkyl benzene sulphonate.

The response cut-off was at 75%.

Example 14

The detergent-dispersant additive of Example 9 was replaced with

Sodium alkyl benzene sulphonate.

The response cut-off was at 70%.

The materials referred to in the foregoing by their trade names or registered trademarks can be described as follows:

Irgalite Fast Brilliant Blue GLS is a phthalocyanine pigment made by Geigy,
Microlith Bordeaux RT and
Microlith Green GT are pigments coated with Staybelite Ester 10 resin, made by Ciba,
Staybelite Ester 10 is the ester of a hydrogenated rosin made by Hercules Powder Co.,
Pentacite P–423 is a pentaerythritol resin made by Reichold Chemicals,
Superbeckosol 1352 is an oil modified isophthalic alkyd resin made by Reichold Chemicals,
Shell X55 is a substantially aliphatic solvent, sp. gr. 0.72, boiling range 58°–140° C., KB value 40, made by the Shell Co.
Shell X4 is a substantially aliphatic solvent, sp. gr. 0.67, boiling range 58°–70° C., KB value 30, made by the Shell Co.
Shellsol T is an aliphatic hydrocarbon solvent, sp. gr. 0.76, boiling range 180°–207° C., KB value 26, made by the Shell Co.
Isopar H is an isoparaffinic hydrocarbon solvent, sp. gr. 0.757, boiling range 340°–380° F., KB value 26, made by Humble Oil and Refining Co.
Mobilgrease No. 5 is a wheel bearing grease made by the Vacuum Oil Co.
Ampol automative oil SAE raitng 20/20W is made by Ampol Oil, Australia.
Shell X100 SAE rating 40 is made by the Shell Co.

Valvoline Super HPO SAE rating 30 is made by Valvoline Oil, Pennsylvania.

BP Energol HD–S3, SAE rating 20 is made by BP Australia.

Valvoline Crystal is a pure mineral oil made by Valvoline Oil, Pennsylvania.

What we claim is:

1. A liquid developer for rendering visible in the reverse sense electrostatic patterns contained on a surface in the form of negative electrostatic charges of varying magnitude which developer consists of a hydrocarbon carrier liquid having a volume resistivity in excess of 10^9 ohm cm. and a dielectric constant of less than 3 having suspended therein toner particles to be deposited electrostatically and having dissolved therein a sensitizing agent incapable of being deposited electrostatically from said carrier liquid, characterized by said toner particles being substantially insensitive to attraction and repulsion by said electrostatic charges when suspended in said carrier liquid in absence of said sensitizing agent, further characterized by said sensitizing agent dissolved in said carrier liquid creating an environment of positive polarity around said toner particles suspended in said carrier liquid thereby sensitizing and urging said toner particles to be deposited electrostatically and further characterized by said toner particles being sensitized by said sensitizing agent to such degree that toner deposition takes place only onto such areas defined by said electrostatic pattern where the intensity of said negative electrostatic charges has been reduced by exposure to electromagnetic radiation by at least 70% of the maximum magnitude of such charges present on said surface, wherein the proportion of said toner particles ranges from 0.1 to 10 parts by weight of said particles to 100 parts of said carrier liquid and wherein said sensitizing agent is a mineral oil containing from 0.5 to 2.0% by volume oxidation inhibiting additive and from 1.0 to 20.0% by volume detergent-dispersant additive, said sensitizing agent being dissolved in said carrier liquid in the proportion of at least 0.01 part by weight of said sensitizing agent to 100 parts of said carrier liquid but wherein the quantity of said sensitizing agent dissolved in said carrier liquid is not sufficient to lower the volume resistivity thereof, said oxidation inhibiting additive being selected from the group consisting of phenyl-b-napthylamine and 2,6-di-tert-butyl-alpha-dimethylamino-para-cresol, and said detergent-dispersant additive being sodium naphtha sulphonate.

2. A liquid developer according to claim 1 wherein the toner particles consist of pigment particles having adsorbed thereon a layer of oleoresinous wetting substance, said wetting substance being selected from the group consisting of pentaerythritol resin, oil modified isophthalic alkyd resin and hydrogenated rosin ester.

3. The method of rendering visible in the reverse sense electrostatic patterns contained on a surface in the form of negative electrostatic charges of varying magnitude comprising contacting said surface with a hydrocarbon liquid developer consisting of a carrier liquid having a volume resistivity in excess of 10^9 ohm cm. and a dielectric constant of less than 3 having suspended therein toner particles to be deposited electrostatically and having dissolved therein a sensitizing agent incapable of being deposited electrostatically from said carrier liquid, characterized by said toner particles being substantially insensitive to attraction and repulsion by said electrostatic charges when suspended in said carrier liquid in absence of said sensitizing agent, further characterized by said sensitizing agent dissolved in said carrier liquid creating an environment of positive polarity around said toner particles suspended in said carrier liquid thereby sensitizing and urging said toner particles to be deposited electrostatically and further characterized by said toner particles being sensitized by said sensitizing agent to such degree that toner deposition takes place only on to such areas defined by said electrostatic pattern where the intensity of said negative electrostatic charges has been reduced by exposure to electromagnetic radiation by at least 70% of the maximum magnitude of such charges present on said surface, wherein the proportion of said toner particles ranges from 0.1 to 10 parts by weight of said particles to 100 parts of said carrier liquid and wherein said sensitizing agent is a mineral oil containing from 0.5 to 2.0% by volume oxidation inhibiting additive and from 1.0 to 20.0% by volume detergent-dispersant additive, said sensitizing agent being dissolved in said carrier liquid in the proportion of at least 0.01 part by weight of said sensitizing agent to 100 parts of said carrier liquid but wherein the quantity of said sensitizing agent dissolved in said carrier liquid is not sufficient to lower the volume resistivity thereof, said oxidation inhibiting additive being selected from the group consisting of phenyl-b-napthylamine and 2,6,-di-tert-butyl-alpha-dimethylamino-para-cresol, and said detergent-dispersant additive being sodium naphtha sulphonate.

4. The method of rendering visible in the reverse sense electrostatic patterns according to claim 3 wherein said toner particles consists of pigment particles having adsorbed thereon a layer of oleoresinous wetting substance, said wetting substance being selected from the group consisting of pentaerythritol resin, oil modified isophthalic alkyd resin and hydrogenated rosin ester.

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