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PROCESS OF DEVELOPING ELECTROSTATIC IMAGES

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The present invention refers to an improvement of manufacturing prints by way of the electrophotographic process. More particularly, the invention concerns a new method of transforming the latent electrostatic image obtained into a visible image and fixing the image and/or transferring it onto a transfer sheet.

In an electrophotographic process, the complete or partial discharge of charged semi-conductive layers by means of light rays is used for the production of a latent electrostatic charge image. According to a special electrophotographic process it is possible to produce on a special layer a charge image which is differentiated from the very beginning. In both cases, the charge image must be made visible, it is developed, and the developed image must then be fixed. Development of the latent charge image is effected by means of a powder or by vapors carrying such powder.

In some cases which are of great practical importance, the developed, but not fixed, image has to be transferred onto another material, most generally paper. Further such transfer is practiced with the image produced on the semi-conductive layer carried over onto materials, such as offset plates, fabric, transparent sheet material, plastics etc. Finally, the powder image, mostly a mixture of resin and carbon black, has to be fixed either by burning in (baking) or melting onto the support, or a strong adhesion to the support is provided by means of solvents.

According to known processes there is used for development of the latent image, a powder which preferably consists of a resin/carbon black mixture and a carrier. Preferably, this carrier consists of pulverized glass or metal. When a powder consisting of a mixture of these components is poured over the semi-conductive layer, the inevitable formation of dust which follows is very disagreeable, because of the strong color of these powders. On the other hand, development of the image by means of vapors is sometimes dangerous and leads to images which lack the required sharpness.

The powder image is fixed by means of heat. The required heat fixing temperature lies above the melting point of the powder, which means the temperature is so high that the materials used, especially paper, is likely to become damaged, or the powder image becomes crumbly. Considerable heat is produced in the apparatuses used for practicing the known processes, and this is difficult to control, so that it is undesirable for the small and handy devices for office use. Fixing by means of solvents has the same drawbacks as mentioned in connection with the development with vapors.

Under the present conditions, transfer of the powder image onto another surface requires either electrostatic fields of high voltage or heat. Both methods have certain drawbacks. If strong electrostatic fields are used, the latent charge image is destroyed, so that it cannot be developed again. Further, this process also requires the fixing of the powder on the transfer sheet, which has the undesirable features mentioned above. If the transfer is effected by melting the powder image onto the second support (transfer sheet) by heating the latter, the difficulties will increase as a result of the application of high temperatures. Moreover, the semi-conductive layers

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have a tendency to go over onto the transfer paper. In this case, too, the above described disadvantages resulting from the application of high temperatures have to be considered.

All these drawbacks, which so far have obstructed the general use of the electrophotographic processes hitherto known are eliminated by the present invention. At the same time the sequence of the different process steps (powdering, transfer, fixation) is simplified.

Contrary to hitherto known processes, which make use of physical methods, the development, transfer, and fixation of the image according to the present invention are effected by means of chemical reactions.

According to the method of the present invention development and fixation of the image—or, in case the image is transferred onto another material, transfer and fixation—are effected by chemical reactions, in which the developer powder, i.e. the powder used for the development of the latent electrostatic image, takes an essential part. The developer powder contains one or more reactive chemical groups, which chemically react with one reactive group or several of such reactive groups contained either in the electrophotographic layer, or, in case the image is transferred, in the transfer material, whereby a visible image is formed. To cause this reaction, the reactive groups must be brought into contact with each other. If the image is to be transferred, the method according to the present invention has the further advantage that transfer and fixation are effected in one step. If it should not be sufficient to bring the reactive groups into contact with each other, the reaction may be initiated or speeded up by the application of warmth, humidity, gases or pressure. The developing powder must be capable of being electrostatically attracted by the electrostatic latent image.

It has been found that in some cases the powder has to be charged, which may be effected, e.g., by mixing it in known manner with glass balls. In other cases, such additional charging may be omitted. This fact may be of importance with regard to the quantity of powder to be attracted. For particular situations, attraction and retention by the electrostatic charge image of a great quantity of powder, or of a small quantity of powder may be desirable. If several transfer images are to be produced from one single charge image, a greater quantity of powder may be successively reacted with several transfer papers. On the other hand, it may be desirable to have only a small quantity of powder attracted, so that in a transfer process according to the present invention all of the powder goes over onto the transfer paper and the latent electrostatic image must be dusted again with developer powder. It is a special advantage of this process, that the powder itself is not responsible for a good, strong density of the image, but that the image is produced later on by a chemical process. This way, even small quantities of powder are sufficient, a fact which may be of importance if the charge image has a low charge only. Low charges may occur intentionally or unintentionally, e.g. if a reflex copying process has been used it is capable of attracting a small quantity of powder only.

It has been found that use can be made of the chemical reaction of various metal salts and/or organic compounds containing said reactive groups, and in the following these will be called "reactants." The reactants may either form as the result of the reaction a firmly adherent dyestuff or colored chemical compound, or the reactant contained in the developer powder may be an ingredient of a colored compound which reacts with the reactant contained in the contacting layers only for the purpose of fixation. If one of the reactants is contained in the electrophotographic semi-conductive layer, the further step of fixing can be omitted, because in consequence

of the reaction the image adheres to the surface and is in a visible state. Alternatively, several reactants may be contained in the developer powder itself, which then participate in the reaction. In some cases it is not even necessary to add special reactants to the light sensitive layers, as the substances required for the preparation of the electrophotographic layer may contain or represent the reactants in question. The inorganic salts and/or organic compounds known to be photoconductive substances may contain or represent the necessary reactants. Alternatively, the substances used as binders, e.g. silicone resins, may be used for this purpose.

If additional reactants are required, it is preferable in some cases to disperse them in a protective colloidal solution before embedding them in the transfer material, in order to ensure an even distribution. The developer powder, too, should be selected with regard to a fine grain size. The special rate of fine distribution of the grains may vary, as can be seen from the examples.

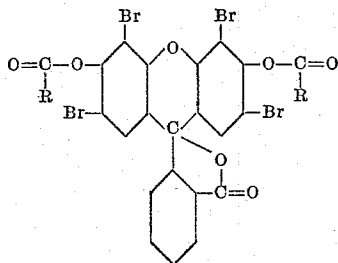
Further it is possible to release the chemical reaction of the reactants by adding a further reactant, e.g. a gas. Such reactions are known to be used, e.g., in diazotype processes, but the application of coupling components known from diazotype processes as reactants in an electrophotographic process according to the present invention is of advantage in that materials of considerably greater light sensitivity are used in the present process.

It is further possible to speed up or even start the chemical reaction by adding suitable catalysts. In some cases this speeding-up or start may be effected by heat and/or pressure and/or humidity. The quantity of heat to be used in practicing the present invention is considerably smaller than that applied in the above described customary processes of melting the resin/carbon black mixture. This means that fewer difficulties arise with regard to the apparatuses used. Nor does the quantity of humidity which may be used in the process of the present invention suffice to make it a "wet-process."

Further it has been found to our surprise that the dye-stuff image obtained by a chemical reaction may be influenced in its color and density by varying the physical and chemical conditions, such as heat, pressure and humidity, which initiate the chemical reaction, when choosing a certain reactant.

Furthermore it has been proved that it is possible to use developer powder, the essential substance of which is a compound containing both reactive groups necessary for the intended reaction. After the electrostatic development, both reactive groups are caused to react with each other by physical-chemical influences, such as heat, pressure, moisture, etc., the reaction product being characterized in that it adheres to the photoelectrical layer. If the image is to be transferred, the physical-chemical influences should be exerted at the very moment, when the transfer material contacts the developer powder adhering loosely to the electrophotographic layer.

Special results have been obtained by using an eosine compound having the formula



in which R stands for a CH_3 , C_2H_5 or C_3H_7 group.

The above mentioned compound has an orange-yellow color. Upon heating, the compound decomposes, while turning deep red. When a mild alkali such as sodium carbonate, sodium stearate, or sodium phosphate is added,

the red color is considerably intensified. In case of transfer, the transfer material can also be soaked with said alkali in the form of a solution or a suspension. A slight moistening of the transfer material with acetone is of advantage.

It has also been found that there can be used a developer powder the essential constituent of which is a compound which is capable of splitting off a part under the influence of physical-chemical methods (heat, pressure, moisture, etc.), the split product adhering firmly to the photoelectrical layer, or in case of transfer to the transfer material.

When heating metal salts of sulphur substituted carbamic acid, e.g. cobalt salts, bismuth salts or iron salts, they split off the sulfide of the respective metal, the color of which is characteristic and which is able to adhere firmly to paper. By addition of various organic compounds, the reaction temperature can be lowered considerably, which is of special advantage when fixing the image. Before heating, such developer substances can also be transferred onto the surface of a second support (transfer sheet) in a manner known per se, and then be treated as described above.

A further method is to choose as the essential substance of the developer powder, a chemical compound which also appears in an isomeric form or several isomeric forms. It has been surprisingly found when using one isomeric form of the compound as a developer powder, that after development, this isomeric form can be converted by means of physical-chemical methods (heat, pressure, moisture, etc.) into its isomer or one of its several isomeric forms and that the isomer formed in this way adheres firmly to the electrophotographic layer, or in case of transfer, to the transfer material. If the developed image is to be transferred, the physical-chemical influence is applied when the developer powder contacts the transfer material, as has already been mentioned above.

If a transfer is desired when using one of the above mentioned methods, it has been found to be of advantage to apply to the transfer material a substance, e.g. a colloid or a synthetic substance, which receives the reaction product and provides a better adhesiveness. A substance of this kind may also be applied to the electrophotographic material or be coated onto the support together with the photoelectrical insulating mass, to the extent the electro-photographic properties are not lost thereby.

Further above it has been said, that in some cases the chemical reaction can be initiated by the influence of gases or vapors. It has now been found that the substance initiating the reaction can also be added in the form of a solution. It has proved advantageous to wipe over the developed image with a cotton pad which has been dampened or soaked with this solution. In this case the reaction and the fixing must take place rapidly enough to avoid blurring of the developed image.

Further it has been found that the transfer paper can not only be coated with a layer containing one of the reactants, but that it is also possible for the purpose of the invention to soak the transfer paper with a solution containing one or more reactants. Thus both surfaces of the paper can be used for transfer, and when transferring an image it is not necessary to watch which side of the prepared material is placed against the developer powder. Furthermore the reactant or reactants can be added in suitable concentration to the paper-mass used in making the paper.

Furthermore, both surfaces of the transfer paper treated as described above can be used as image-receiving surfaces if the paper is made of specially suitable raw materials and certain reactants are used. This two-sided use of transfer paper can be considered if the chemical reaction takes place close to the surface of the transfer-paper and the thus formed reaction product remains fixed to the reaction zone and does not pass through the paper. It has been found that this is possible in some cases without taking special precautions. In some other cases care must

be taken that the degree of humidity in the paper is not too high, and above all, not too much reactive developer powder must be allowed to be transferred.

The quantity of powder (developer powder) adhering electrostatically to the surface of the semi-conductive layer depends on the charge of the semi-conductive layer as well as the charge of the powder resulting from known triboelectric or friction effects. But if the control of these quantities of electrical charge seems to be too difficult the quantity of the reactive developer powder can be diminished by mixing the reactive developer powder with an indifferent substance which should, if possible, have the same electrostatic properties as the reactive powder.

In apparatuses for practicing this method the above stated problem concerning the moisture content can be solved by regulating the degree of moisture of a sponge or the like which moistens the surface of the paper in order to release the chemical reaction with the reactant contained in the developer powder, which is transferred immediately afterwards. In an apparatus for continuous use, the sponge or a like body can, for example, be pulled through a trough containing water, or in some rare cases alcohol or other solvents, and then be given the most suitable degree of moisture by means of a doctor-knife which exerts a variable pressure on the sponge.

Because, as already pointed out, the chemical reaction takes place in some cases only in the presence of, e.g. a certain quantity of moisture or, in other cases, of heat or pressure, it is possible to hold the reactants in admixture with each other in the developer as long as no moisture, heat or pressure is applied and, as a consequence, no reaction of the reactants can take place.

If, for example, the surface of the transfer paper is moistened and is caused to contact the developer powder mixture adhering to the semi-conductive layer, immediate reaction occurs only on the surface of the moistened paper and the reaction mixture remains on the surface of the transfer paper. If in this case reactants are chosen which form a compound insoluble in the original solvent (mostly water) which reaction product, in addition, remains adhering to the surface of the paper and does not diffuse through the paper, the transfer process can be repeated on the opposite face of the paper so that a double-sided copy can be obtained.

The reaction in question can also be caused by application of heat as already mentioned. In this case the transfer paper is warmed to a suitable temperature prior or during its contact with the developer powder mixture adhering to the electrostatic paper.

Furthermore the reaction can be caused by pressure. This pressure must prevail at the moment of contact between the developer powder mixture and the transfer paper. In apparatuses for practicing this method the desired effect can be obtained by conducting the transfer paper and the semiconductor paper which already carries the developer powder mixture in the form of an image, through a pair of pressure-rolls, for example.

Where a double-sided use of the transfer paper which is soaked with one of the reactants, is not possible, the transfer paper may be coated on both sides with the solution of the reactants; but it is obvious that the production of such paper is more complicated.

Further it must be pointed out that the process according to the invention is not only applicable to paper raw material, but also to other suitable raw material.

It can be measurably demonstrated that by the use of developer powders according to the present invention the sensitivity of electrophotographic processes is considerably increased. With the compositions stated in the examples about $\frac{1}{4}$ of the exposure time is required as compared with the customary resin/carbon black mixtures. The sensitivity may be controlled by adding substances to the powder which influence the charging capacity of the powder. This has proved to be of special importance in the production of reflex copies, which are

known to produce a latent image with a relatively low charge potential.

The following examples serve to illustrate the process of the present invention. It is not intended to limit the scope of the present invention to the contents of said examples.

Examples

(1) As developer, the sodium salt of pyrrolidino-carbamate in form of a powder is used. Mixing with glass balls for charging the powder is not absolutely necessary. A ZnO-layer charged with 9 kv. was exposed under a positive pattern for 1 second. Subsequently development was effected by means of a cascade process. The transfer material was then coated with a 5% solution of ammonium ferric sulfate and dried. Shortly before use, the paper was slightly dampened and then contacted with the electrophotographic paper, to which the developer substance was already adhering. A brownish-black dye-stuff image was obtained.

(2) As developer substance, piperidine-carbamate was used. The process was conducted in principle, in the same manner as in Example 1.

For transferring the image, barytic paper which had been treated with a 10% ammonium ferric sulfate solution was used. The iron salt of the substituted dithiocarbamic acid obtained by reaction was also of a deep brownish-black color.

(3) A mixture comprising 95% of glass balls and 5% of iron stearate was used as developer. In principle it was proceeded as described in Example 1. Iron stearate is particularly suitable for electrostatic development.

The transfer material was produced by coating a paper base with a saturated alcoholic solution of gallic acid and subsequent drying. Before contacting it with the iron stearate adhering to the ZnO-paper, it had to be wetted with an 80% aqueous alcohol. The neutral black color was then obtained by the formation of the iron salt of the gallic acid. By heating the transfer material, reaction could be speeded up.

(4) A diazo compound of the amino carbazole as described in the German patent specification No. 523,259 is mixed with glass balls in the ratio of 4:96. The latent electrophotographic image is developed with the above mentioned diazo compound. For rendering more visible and for better fixation of the powder image thus obtained, it is moistened with a solution of β -naphthol, borax and water. The image is obtained immediately.

(5) A mixture described in U.S. patent specification No. 2,487,034, Example 1, comprising 2,8-dihydroxynaphthalene-6-sulfonic acid, N-phenylaniline-p-diazonium acid sulfate, citric acid, thiourea and zinc chloride is mixed with glass balls in the ratio of about 4:96. The mixture thus obtained is then poured over the latent electrophotographic image.

The image is rendered visible and fixed by bringing it into ammonia vapor.

(6) A mixture comprising the zinc chloride double salt of the diazo compound from 5-amino-2-benzoyl-amino-1,4-diethoxy benzene and primary sodium phosphate according to German patent specification No. 684,334 is mixed with glass balls in the ratio of 4:96 and then poured over the electrophotographic latent image.

A transfer paper is coated with phloroglucinol. Subsequently it is slightly moistened with a solution containing sodium chloride, sodium acetate and tartaric acid and is then contacted with the powdered image. The visible colored image is obtained on this second surface.

(7) The process of Example 6 can also be executed by incorporating phloroglucinol, finely distributed in a colloid, for example a watersoluble colloid such as the sodium salt of alginic acid, into the electrophotographic layer, or by coating the electrophotographic layer with such phloroglucinol-colloid combination. Powdering of the latent electrostatic image is executed as described

above. Subsequently, the image has to be moistened with an aqueous solution consisting of sodium chloride, sodium acetate and tartaric acid.

(8) Developer: p-amino-diphenylamine-hydrochloride. Transfer-paper: soaked in or coated with a solution of:

VCl ₅ -----	g--	0.25
KHSO ₄ -----	g--	20.00
K ₂ S ₂ O ₈ -----	g--	15.00
H ₂ O -----	ml--	100.00

The developer which may be mixed in a proportion of 25:1 with glass balls, forms a fine powder and is attracted by the still electrostatically charged areas of the semi-conductive layer (ZnO-layer). The prepared transfer paper is moistened shortly before use and brought into slight contact with the powdered semi-conductive layer. Reaction takes place immediately. During the drying-process of the slightly moistened paper the color shade—aniline black has been formed—becomes still somewhat deeper. The reaction time and the drying time can be shortened by passing the developed transfer paper adjacent a heat-source. The VCl₅ serves as a catalyst, the KHSO₄ adjusts the pH-value, and the K₂S₂O₈ acts as an oxidizing agent.

(9) Developer: as in Example 8. Transfer-paper:

(A) 40% (NH ₄) ₂ S ₂ O ₈ -solution.	
(B) VCl ₅ -----	g-- 0.5
KHSO ₄ -----	g-- 20.0
H ₂ O -----	ml-- 150.0

The transfer paper is obtained by the following process: The paper raw material is treated first with the above solution (A), dried and then treated with the solution (B). Thus it is possible to obtain a higher S₂O₈ concentration, which is necessary for the oxidation of the p-amino-diphenylamine-hydrochloride.

(10) Developer: C₆H₅NH₂—HCl. Transfer-paper:

K ₂ Cr ₂ O ₇ -----	g--	2.0
CuSO ₄ -----	g--	0.2
KHSO ₄ -----	g--	0.5
H ₂ O -----	ml--	100.0

The aniline hydrochloride (or aniline sulfate) can be mixed with glass-balls. The transfer paper is soaked in or coated with the above aqueous solution. After slightly moistening the paper, reaction to a deep black dye-stuff (black-green) takes place. The K₂Cr₂O₇ serves as an oxidizing agent, the CuSO₄ as a catalyst and the KHSO₄ for the regulation of the pH-value.

(11) Developer:

K ₂ Cr ₂ O ₇ -----	2.0 g.
CuSO ₄ -----	0.2 g.
KHSO ₄ -----	0.5 g.

Transfer-paper:

C ₆ H ₅ NH ₂ —HCl -----	g--	20.0
C ₂ H ₅ OH -----	ml--	100.0

The dry developer mixture can be applied with or without glass balls. The transfer paper is coated with the aniline solution.

Otherwise the process is as described in Example 10.

Other amines that can be used in the manner of the above examples are p-amino-p'-hydroxy-diphenyl-amine, p-dimethyl-amino-p'-hydroxy-diphenyl-amine, and p-amino-methyl-diphenyl-amine. As oxidizing agents chlorates, chromates and permanganates can also be used, and copper ions in general as well as iron ions and OsO₄ are further examples of suitable catalysts.

(12) The developer used was pulverized copper sulfate which could be mixed with glass balls. Even without glass balls good results were obtained. Development of the electrostatically charged and exposed zinc oxide layer was effected by cascading.

As transfer paper a paper was used which was first soaked in a 10% sodium sulfide solution and then dried. Shortly before its use, i.e. before contacting it with the copper salt adhering to the zinc oxide layer, the transfer paper was slightly moistened on its surface by means of a sponge. A deep black color was formed, the color being due to the copper sulfide formed.

The same results could be obtained by using lead nitrate or silver nitrate instead of copper salts. Both salts were very well suited for the electrostatic development. Soluble Co, Cd, As, Sb, Mn, Ni and Hg salts can also be used, and polysulfides as well as sulfides, especially those of the alkali metal group.

What we claim is:

The process of developing electrostatic images and fixing them on a support, which process includes the steps of applying powdered iron stearate to an electrostatic image to cause the powder to electrostatically adhere to the charged portions of the image to form a powder image, and then contacting the powder image with a transfer sheet wet with an alcoholic solution of gallic acid to cause the iron stearate of the powder image to react with the gallic acid and form a black reaction product adherently held on the transfer sheet in the shape of the powder image.

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