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METHOD FOR RETOUCHING AN ELECTROPHOTOGRAPHIC OFFSET MASTER PLATE
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FIG. 1

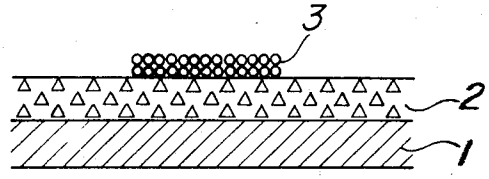


FIG. 2

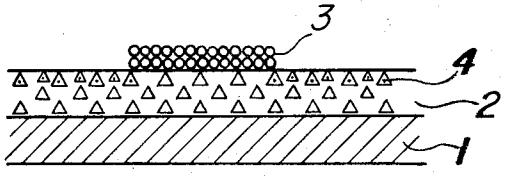


FIG. 3

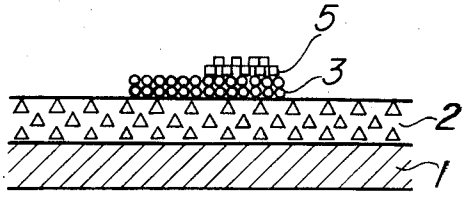
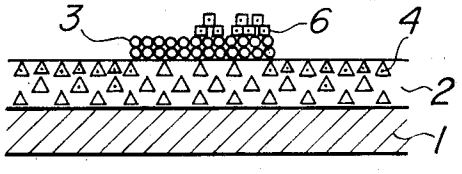


FIG. 4



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METHOD FOR RETOUCHING AN ELECTROPHOTOGRAPHIC OFFSET MASTER PLATE

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U.S. Cl. 117—37 R 6 Claims

ABSTRACT OF THE DISCLOSURE

An electrophotographic offset master plate can be retouched by applying a solution to areas of the plate which are to be deleted from printed products, prior to rendering non-imaged portions ink-repellent. The solution contains metal compound which reacts with rendering solution (which renders the non-imaged portions ink-repellent and water-receptive) comprising water soluble metal salt of hexacyano metallic acid and/or ammoniumphosphate to produce hydrophilic water insoluble precipitates. In spite of uniform wiping of the surface with rendering solution, the imaged portions are still oleophilic while non-imaged portions become hydrophilic. This is because that near the non-imaged surface there exist materials which react with rendering solution to form hydrophilic and water insoluble precipitates e.g. $K_2Zn_3[Fe(CN)_6]_2$, $ZnNH_4PO_4$ etc., while near the imaged surface such materials don't exist.

This invention relates to a method for retouching an offset printing plate (master plate) produced by electrophotographic method. The offset printing plate according to electro-photographic method can be easily produced by combination of production of usual electro-photograph and application of a rendering solution (which renders the non-imaged portions ink-repellent and water-receptive) to the surface having thereon reproduced image, namely, without any high skilled labour.

For example, photoconductive zinc oxide and a binder are applied to a base paper having length stability and water resisting property to form a photoconductive layer. Electric charge is placed on said layer by corona discharge, for example, and the surface is exposed to light image in darkness to cause the charge to be dissipated in areas which light strikes and to be left in areas which light does not strike, thus forming an electrostatic latent image. Then, the surface having the latent image is dusted with a pigment powder carrying a charge or immersed in an insulating liquid in which said powder is dispersed to attract the powder to the latent image area to make the latent image visible.

Generally, the pigment powder used as a developer is covered with a resin and is fixed on the substrate while heat-fusing or volatilization of solvent.

Since the pigment powder is covered with a resin, the developed image portion has oleophilic property. In order to utilize thus obtained reproduction of electrophotography as an offset printing plate (a master plate), it is necessary to make the non-imaged area hydrophilic. One method therefore comprises wetting the reproduction surface with a rendering solution, in which compounds such as potassium ferrocyanide, sodium ferrocyanide, potassium ferricyanide, ammonium phosphate, etc. are dissolved, to cause reaction with zinc oxide, thereby forming a film of water insoluble precipitate e.g., $K_2Zn_3[Fe(CN)_6]_2$; $ZnNH_4PO_4$, etc. on the area which has been made hydrophilic. The wetting may be carried out by merely wiping the surface with an absorbent cotton or a gauze impregnated with the rendering solution.

An object of this invention is to provide a method for retouching the offset printing plate obtained as mentioned above and more particularly is to provide a method for removing only the areas of the plate which are not desired to be printed or removing fogged area or stains.

FIG. 1 shows a cross-sectional view of an electrophotographic paper on which an image is formed.

FIG. 2 shows a cross-sectional view of an offset master plate made from said electrophotographic paper by imparting hydrophilic property to paper.

FIG. 3 shows a cross-sectional view of said offset master plate in which the retouching agent of this invention is applied to the surface of the image on said master plate.

FIG. 4 shows a cross-sectional view of the offset master plate obtained by imparting hydrophilic property to the master plate of FIG. 3.

In FIG. 1, **1** is a substrate (paper), **2** is a photoconductive insulating layer comprising zinc oxide and resin binder and **3** is a pigment powder layer stuck to image area. In the non-image area, the rendering solution reacts with zinc oxide to form hydrophilic and water insoluble precipitate, e.g., $K_2Zn_3[Fe(CN)_6]_2$, $ZnNH_4PO_4$, etc. Therefore, in spite of uniform wiping of the surface with said solution, the non-image area is made hydrophilic, while on the surface of the image area, such materials as react with said solution to form hydrophilic and water insoluble precipitate are not present. This is shown in FIG. 2, wherein **4** shows zinc compound which is hydrophilic and water insoluble due to reaction with the rendering solution.

In order to prevent printing of the image area in which pigment powder layer is formed, the simplest and surest way is to brush off the pigment powder layer before fixing in dry development procedure. When fixation is completed (after heat fusing in dry development and after self fixation in wet development), it is difficult to brush off the pigment powder. Therefore, a layer capable of reacting with the rendering solution to form hydrophilic and water insoluble precipitate is provided on the surface of the pigment powder layer to completely cover the pigment powder layer with said precipitate. In case of using a rendering solution containing water insoluble metal hexacyanide salts (e.g. alkali metal salts of hexa- cyanocobaltate acid (II) and (III), ferrocyanide and ferricyanide) or ammonium phosphate $[(NH_4)_2HPO_4]$, a solution in which a compound of a metal element selected from the group consisting of Be, Mg, Zn, Hg, Cu, Ag, Al, Tl, Th, Sn, Pb, Bi, Zr, Co, Cr, Cd, Ni, Fe, Mn and Ga is dissolved (for example, in water, methanol and water-methanol) or said solution to which a very small amount of resin which is initially water soluble, but becomes water-insoluble when the solution is made to a dry film is optionally added is applied to the area to be removed and air-dried or heat-dried, thereby forming the layer **5** in FIG. 3. The whole surface of the master plate is then treated with an absorbent cotton or a gauze impregnated with a rendering solution to cause layer **5** in FIG. 3 to react with said solution to form a hydrophilic and water insoluble precipitate as shown by **6** in FIG. 4 as well as zinc oxide of non-image area forms a hydrophilic and water insoluble precipitate. As mentioned above, the areas shown by **4** and **6** in FIG. 4 are made hydrophilic and do not receive ink. Thus, a retouched printing plate is produced.

The above-mentioned metal elements may generally be used in the form of chlorides or nitrates to form aqueous or alcohol solutions thereof. The examples of these compounds are $BeCl_2$, $MgCl_2$, $ZnCl_2$, $Hg(ClO_3)$, $CuCl_2 \cdot 2H_2O$, $AgNO_3$, AlC_3, TlCl, $Th(NO_3)_4 \cdot 4H_2O$, $SnCl_2$, $PbCl_2$, $Pb(CH_3COO)_2$, $BiCl_3$, $ZrCl_4$, $CoCl_2 \cdot 6H_2O$, $CrCl_3$, $CdCl_2$, $Ni(NO_3)_2 \cdot 6H_2O$, $FeCl_3$, $MnCl_2$, $GaCl_3$, etc.

The concentration of said compounds in the solution may be varied depending upon kind of the compounds, but, in general, may be in the range of 1–30% by weight in terms of metal element.

In case of using a rendering solution containing metal hexacyanide salt and/or ammonium phosphate, compounds of alkali metals and some of alkaline earth metals (Ca, Sr, Ba) do not produce water insoluble precipitate reacting with said solution, hence cannot be used as a retouching agent. For example, Ca reacts with potassium ferrocyanide to produce $Ca_3[Fe(CN)_6] \cdot 12\ H_2O$ which is water soluble compound. Furthermore, Ca reacts with ammonium phosphate to produce $CaHPO_4$ which is water insoluble in a neutral solution, but water soluble under acidic condition. On the contrary, with reference to metal compounds which can be used as a retouching agent such as Zn, Fe and Co, they react with said solution to form $K_2Zn_3[Fe(CN)_6]_2$, $ZnNH_4PO_4$, $Fe_4[Fe(CN)_6]_3$, $FePO_4$, $Co_2[Fe(CN)_6]$ and $CoNH_4PO_4$ which are all stable precipitates, and which are insoluble in water.

As explained above, according to this invention, retouching of offset master plate obtained by electro-photography can be accomplished by forming water insoluble and hydrophilic precipitate on the areas of offset master plate to be retouched prior to making the offset master plate hydrophilic with metal hexacyanide salt and/or ammonium phosphate. By this method, not only an electrostatically developed image obtained by especially wet developing can be freely and completely retouched regardless of the original, but also fog and stains on the master plate which have been sometimes caused can completely be removed. Furthermore, these can be accomplished by simple procedure.

The following specific examples will serve to illustrate this invention but are not to be considered limiting.

EXAMPLE 1

10 grams of $Zn(NO_3)_2 \cdot 6H_2O$ was dissolved in a mixture of 50 g. of water and 40 g. of methanol and thus obtained solution was used as a retouching agent. The image area to be removed in a master plate obtained by liquid developing method of electro-photography was applied with said retouching agent and dried. Thereafter, the whole surface was treated with a rendering solution which was prepared by dissolving 120 g. of

$K_4Fe(CN)_6 \cdot 3H_2O$, 370 g. of $NH_4H_2PO_4$

130 g. of $(NH_4)_2HPO_4$ and 50 g. of 80% H_3PO_4 in water to make the total volume 10 l. Then, offset printing was carried out using thus treated master plate.

The area to be intended to remove was not printed at all and no stains occurred.

EXAMPLE 2

30 grams of $Zn(NO_3)_2 \cdot 6H_2O$ was dissolved in 70 g. of methanol and thus obtained solution was used as a retouching agent. The treatment of Example 1 was repeated and offset printing was carried out. The area to be removed was not printed at all and no stains were caused. Even when the drying after application of retouching agent was carried out by spontaneous drying at room temperature the master plate was excellent in printing resistance and no defects were caused by about 1000 sheet printing.

EXAMPLE 3

The procedure of Example 2 was repeated except that $ZnCl_2$ was used in place of $Zn(NO_3)_2 \cdot 6H_2O$ to obtain the similar good results.

EXAMPLE 4

The procedure of Example 2 was repeated except that $Zn(NO_3)_2 \cdot 6H_2O$ was replaced by $Zn(CH_3COO)_2$ to obtain the similar good results.

EXAMPLE 5

The procedure of Example 2 was repeated except that a solution prepared by dissolving 3 g. of $FeCl_3 \cdot 6H_2O$ in 4 g. of water and 18 g. of methanol was used as a retouching agent to obtain the similar good results with Examples 2–4.

Said retouching agent was colored one and the retouched area was recognized at a glance.

EXAMPLE 6

The procedure of Example 2 was repeated except that a solution obtained by dissolving 5 g. of $SnCl_2 \cdot 2H_2O$ in a mixture of 5 g. of water and 20 g. of methanol was used as a retouching agent to obtain the similar good results.

EXAMPLE 7

The procedure of Example 2 was repeated except that a solution obtained by dissolving 3 g. of $AgNO_3$ in a mixture of 5 g. of water and 20 g. of methanol was used as a retouching agent to obtain the similar good results.

EXAMPLE 8

The procedure of Example 2 was repeated except that a solution obtained by dissolving 3 g. of $AlCl_3$ in a mixture of 5 g. of water and 20 g. of methanol was used as a retouching agent to obtain the similar good results.

EXAMPLE 9

The procedure of Example 2 was repeated except that a solution obtained by dissolving 4 g. of $MgCl_2$ in a mixture of 5 g. of water and 20 g. of methanol was used as a retouching agent to obtain the similar good results.

EXAMPLE 10

The procedure of Example 2 was repeated except that a solution obtained by dissolving 4 g. of $MnCl_2$ in a mixture of 5 g. of water and 20 g. of methanol was used as a retouching agent to obtain the similar good results.

EXAMPLE 11

1.0 gram of 25% xylene toluene solution of vinyl acetate resin (trade name: Sebian 730 manufactured by Dainihon Celluloid K.K.) was added to a mixture comprising 0.2 g. of H_3PO_4 (concentration 85%), 50 g. of H_2O and 30 g. of methanol. 3.0 grams of $ZnCl_2$ was dissolved therein and the resultant solution was used as a retouching agent.

After completion of electrophotographic dry development, the retouching agent well adhered to the surface of image which was heat fixed. Good results were obtained by the same treatment as mentioned in the preceding examples.

EXAMPLE 12

0.2 gram of Aniline Blue was dissolved in the retouching agents of Examples 2, 3 and 4 to color them. These were used as retouching agents. The area to be retouched was dyed in blue and the retouched area was recognized at a glance. Furthermore, the similar good results were obtained.

In the above examples, drying was carried out by hot air drying with hair drier or at room temperature.

What is claimed is:

1. In a method for retouching an electrophotographic offset master plate to which hydrophilic property is imparted with a solution comprising a member of the group consisting of water soluble metal hexacyanide salts and ammonium phosphate in a solvent selected from the group consisting of water and alcohol, the improvement comprising treating said plate with a solution in a member of the group consisting of water and alcohol of a metal compound capable of reacting with said solution of water soluble metal hexacyanide salt or ammonium phosphate to form a hydrophilic and water insoluble precipitate in the areas of the plate which are to be removed and thereafter treating the plate with said solution of water soluble

metal hexacyanide salt or ammonium phosphate to form said precipitate.

2. A method for retouching the master plate according to claim 1, wherein the metal of the metal compound is a member selected from the group consisting of Be, Mg, Zn, Hg, In, Cu, Ag, Al, Tl, Th, Sn, Pb, Bi, Zr, Co, Cr, Cd, Ni, Fe, Mn and Ga.

3. A method according to claim 1, wherein the metal compound is a chloride or a nitrate of the metal.

4. A process according to claim 1 wherein the plate is dried prior to treating with said solution of water soluble metal hexacyanide salt or ammonium salt.

5. A process according to claim 1 wherein the solvent of the solution is water, methanol or a mixture of water and methanol.

6. A process according to claim 1 wherein said precipitate is a hexacyanide.

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U.S. Cl. X.R.

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