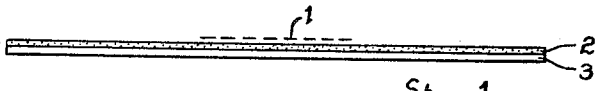
Oct. 15, 1968 K. A. METCALFE ETAL 3,406,061

METHOD OF CONDITIONING PHOTOCONDUCTOR SURFACES

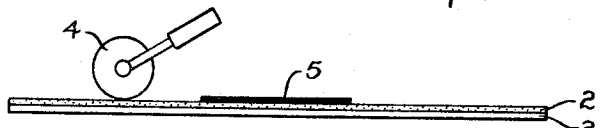
Filed Dec. 8, 1964

FIG. 1[a]



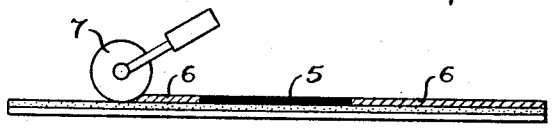
Step 1

FIG. 1[b]



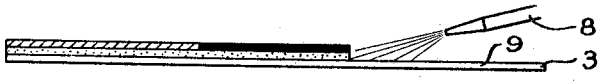
Step 2

FIG. 1[c]



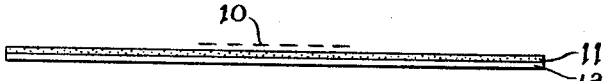
Step 3

FIG. 1[d]



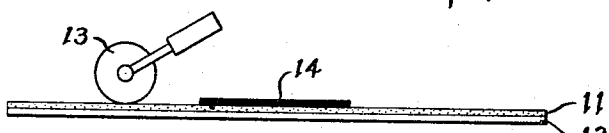
Step 4

FIG. 2[a]



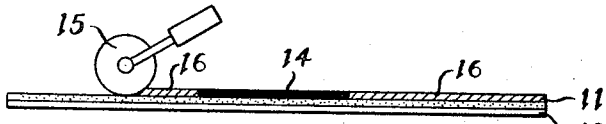
Step 1

FIG. 2[b]



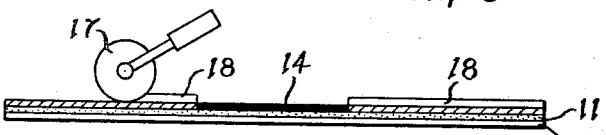
Step 2

FIG. 2[c]



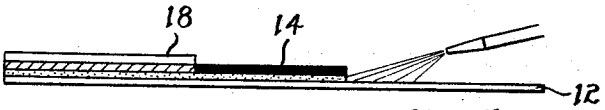
Step 3

FIG. 2[d]



Step 4

FIG. 2[e]



Step 5

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3,406,061

METHOD OF CONDITIONING PHOTOCONDUCTOR SURFACES

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Claims priority, application Australia, Dec. 13, 1963, 38,833/63
10 Claims. (Cl. 96—1)

ABSTRACT OF THE DISCLOSURE

A method of conditioning photoconductor surfaces in which the image is developed in one liquid medium and a second liquid medium is then applied which is not compatible with the first medium so that both liquids wet different parts of the image and then applying a decomposing agent selective to one of the liquids to decompose the photoconductor in contact with the liquid.

Drawing

FIG. 1(*a*)–1(*b*) show the four sequential steps of a method provided in accordance with one embodiment of the invention; and

FIGS. 2(*a*)–(*e*) show the five steps of a method provided in accordance with a second embodiment of the invention.

This invention relates to a method of conditioning photoconductor surfaces.

Photoconductor surfaces for the production of xerographic images usually comprise a photoconductor which is evaporated or otherwise coated on to a surface or alternatively a particulate photoconductor is embedded in an insulating film-forming matrix, the photoconductor in each case being capable of receiving a charge which can then be modified by a light image or the like and the electrostatic image so produced developed by contacting the surface with developer particles having the correct charge.

Photoconductor surfaces of this type have been used for very many purposes such as for the production of visible images, for the formation of printing blocks, or for the manufacture of printed circuits, the various processes utilizing the photoconductor surface in different ways to attain the particular objective.

It is already well known to produce an image on a photoconductor and to then develop the image with a resist developer capable of preventing attack of the photoconductor in the areas beneath the resist so that the remainder of the photoconductor could be removed by dissolving or etching same away.

The present invention relates generally to this type type of process but has a very much wider application and can be used wherever it is desirable to remove a photoconductor film to give access to the surface beneath for etching or for any other purpose.

The method of conditioning photoconductor surfaces according to our invention consists in producing an electrostatic latent image on a photoconductor surface, then developing the electrostatic latent image with a first liquid developer at least part of which has an affinity for the charged areas of the latent electrostatic image to be drawn and held thereto, then while the first liquid developer remains on the photoconductor surface wetting the surface with a second liquid which is not compatible with the first liquid, decomposing the photoconductor by contact with a decomposing agent which is selective to one

of the said liquids to be accepted thereby, and then removing the photoconductor where so decomposed.

According to one method, the second liquid, which is not compatible with the first liquid developer, contains a decomposing agent for the photoconductor so that on application of this liquid the photoconductor is decomposed where contacted by the liquid.

According to another method, the decomposing liquid is applied to the surface after application of the second liquid, which decomposing liquid is chosen to be selective to one of the liquids only to combine with that liquid and to decompose the photoconductor where contacted by this decomposing liquid.

By the above method when using a pure liquid developer, development apparently takes place through differential charging of the first liquid in relation to the electrostatic image so that the liquid is attracted to the charged image areas, and therefore if while retaining the first liquid in place, the surface is contacted with a second liquid which is immiscible with the first liquid, the second liquid will be deposited on those areas which do not contain any of the first liquid, and therefore if the second liquid is of the decomposing type, or carries a decomposing medium, or has a decomposing medium subsequently applied to one of the liquids which is compatible with that liquid, the photoconductor surface on which it exists will be modified so that it can be readily removed.

The method of protecting the first liquid against removal during the subsequent application of the second liquid is to carry out the two processes with sufficient rapidity to prevent the first liquid from leaving the area concerned and of course under such conditions that the electrostatic image is not destroyed. This can be achieved, for example, by making the first liquid an insulator and having the electrostatic field hold the first liquid in place.

To facilitate the locating of the first liquid after it has been deposited, this liquid may be of a type having a high viscosity, such as a silicone, which will then tend to remain in position, or alternatively a developer medium can be carried down with the liquid to be co-deposited therewith and thereby to ensure that the liquid is held in place, the developer material for this purpose preferably being such that it can absorb the liquid to ensure better holding of same.

After deposition of the second liquid and the decomposing medium, the surface on which it is then acting can be wiped away or washed away in any desired manner, and it will be found that if this invention is used such photoconductors as selenium or zinc oxide can be readily removed by utilizing a 5 to 10 percent solution of potassium hydroxide, sodium sulphide or sodium hydroxide in ethyl alcohol or methyl alcohol or diacetone or other higher alcohol.

It has been found that any substances of the character of those mentioned can be advantageously used for this invention without being limited to the substances mentioned.

According to a preferred method of carrying out the invention for instance a zinc oxide or selenium coating on paper or metal is produced in the already well known manner and this is charged and exposed to an image so that an electrostatic latent image is formed on the surface.

This image is then developed by means of a liquid developer comprising either a viscous high boiling point developer liquid having an electrical resistivity in excess of 10^9 ohm centimetre and a dielectric constant less than 3 which may carry a particulate material such as a resin or the like or a resin or other bonding medium in conjunction with a pigment particle, the resin or the like preferably being so selected that it absorbs some of the

insulating liquid to hold it during the subsequent process.

After developing the image in this way and while the image is still wet the surface is subjected to a mixture comprising a polar substance such as an alcohol and an insulating liquid which can be the same liquid used for the first part of the process, but these two liquids must not be miscible so that the polar liquid will then be repelled by the insulating liquid held on the image and will only be able to act to wet the remaining surface.

A caustic medium can be placed into the alcohol so that the photoconductor surface is decomposed where the caustic acts on it, or an additional processing can be carried out by subjecting the surface to a caustic mixture dissolved in alcohol or other polar liquid, after first treating the surface with the mixture of polar and non-polar liquid.

The decomposed surface can then be readily removed by means of a mechanical action such as the use of a jet of water or an abrasive, it being found that the effect of the decomposing of the surface being to render is readily removable.

In the case of selenium this avoids the necessity of using carbon bisulphide as the solvent medium and therefore a much safer and better process results.

For the invention to be fully appreciated various methods of applying it will now be described with reference to the accompanying drawings, but it is to be clear that variations in these methods can be carried out within the appended claims.

In the drawings FIG. 1 shows a simple method in which a minimum number of steps are used, step 1 consisting in supporting a charge **1** on a photoconductor surface **2** on a backing member **3**, the photoconductor surface taking any of the known forms such as a film of vacuum deposited selenium on a base, or a zinc oxide photoconductor embedded in a resin film or the like applied to a thin aluminum or paper backing or other support, the charge **1** being applied in any manner such as by first subjecting the photoconductor surface to a corona discharge and then light-bleeding the surface through a negative or the like to leave a latent electrostatic image of the pattern which it is desired to produce.

Step 2 consists in developing the latent electrostatic image with a first liquid which may be achieved by passing a roller **4** over the surface, the roller being pervious and carrying the necessary developing liquid so that a developed image **5** is produced on the photoconductor **2** which will be held thereto by the charge.

Step 3 consists in applying the second liquid **6** thereto preferably by means of a roller **7** which carries the liquid, the wetting of the photoconductor by this liquid taking place only in those areas where the developer **5** was not attracted to and held on the photoconductor surface, this being because the two liquids must be non-compatible so that the first applied liquid **5** controls the deposition of the second liquid **6**.

The liquid **6** in this case has in it a decomposing agent for the photoconductor and therefore after it is applied to the surface the photoconductor will be decomposed, and in step 4 is then shown how by means of a jet of water or other liquid, applied with sufficient force, the second liquid and the decomposed photoconductor are removed.

The jet or brush is designated **8** and the area from which the photoconductor has been removed is designated **9**.

The jet may of course remove both of the liquids, that is the first liquid **5** and the second liquid **6**, but as the first liquid **5** did not contain a decomposing agent it will be obvious that the photoconductor which is protected thereby will remain intact and therefore during the washing operation, even if both liquids are removed, the one area will have the photoconductor removed because of the decomposing action while the other area will still retain the photoconductor.

In this way of course a master can be readily produced using for instance an aluminum base or plastic base or film base on which the photoconductor surface, such as an organic photoconductor surface, was held, the process permitting the master to be continuously produced in that the first liquid is simply put down onto the developed image, the second liquid containing the decomposing substance is then applied, and after decomposition has taken place the liquids are removed by washing or abrasion or the like, whereupon a master will result which has areas where the aluminum or plastic is exposed and areas where the photoconductor remains in place, these areas then defining an image which can immediately be used in offset printing or for any other further processing if that is required.

The advantage of the process of course is that there is no drying between the steps and the whole process can be carried out in the shortest possible time.

In the embodiments shown in FIG. 2, step 1 shows the latent electrostatic image **10** on a photoconductor **11** on a base **12**, step 2 showing how the roller **13** applies the developer **14** to the latent electrostatic image **10**, step 3 showing the application by means of the roller **15** of the second liquid **16** which in this case can simply be a polar substance, the first developer **14** having been an insulating liquid, both liquids in this case being retained on the surface according to the original electrostatic pattern, step 4 showing how by means of a roller **17** a decomposing liquid **18** can be applied to the surface, the decomposing liquid of course in this case being given an affinity for or solubility in the liquid **16** so that it is absorbed or held by this liquid and therefore causes the liquid to become a decomposing agent to act on the photoconductor in the area concerned, step 5 showing how by means of the jet **19** the liquid and photoconductor are removed from the area **20** whereas the area **21** will retain the photoconductor because of the protection afforded by the liquid **14**.

It will be obvious that using this further step, and first of all using two selective liquids on the photoconductor surface, the decomposing agent could be made compatible with either the liquid **16** or the liquid **14** and therefore instead of it being absorbed by the liquid **16** as shown in FIG. 2 it could be absorbed by the insulating liquid **14** so that the opposite areas of the photoconductor surface would then be removed.

Example 1.—The paper, plastic, metal or other sheet which it is desired to use as a backing is first coated with a photoconductive layer having the following composition:

	Grams
Photoconductive zinc oxide (such as Durham Special supplied by Harrisons Ramsay Ltd.)	100
Resin, long oil alkyl (such as Rhodene M8 alkyd resin or Lustrasol 180 resin, Reichold Chemical Corp.	30
Dyes:	
Rose Bengal	0.1
Sod. fluorescein	0.01
Brilliant green	0.01
Driers	0.02
Toluene	50

After curing for 6–8 hours at 140° F. the coating is ready for use in the selective process of the present invention. The sheet is charged electrostatically at a field strength of 10 kv./inch to produce an overall surface charge equivalent to approximately 300 v. potential.

The sheet is then exposed to the desired subject and developed in a developer prepared as follows:

Shellsol T—90 parts by volume (a hydrocarbon liquid by the Shell Company)

Silicone fluid—10 parts by volume (such as Dow Corning silicone fluid, viscosity 200 cps.)

These ingredients are blended together to produce a

liquid developer in which the silicone fluid will deposit on the image areas to leave a viscous image.

The sheet is developed face down in a metal dish or with metal rollers to produce maximum deposition in the areas of maximum density. This involves 30 seconds to 1 minute in the dish and 4 passes with the rollers.

The wet sheet is then rinsed in clear Shellsol T to remove excess and while wet is placed in an emulsion of Shellsol T and water having the following composition:

	MI.
Shellsol T	60
Water	40
Wetting agent, Nonidet P40 (Shell Company)	1

These liquids are shaken vigorously in a shaking vessel to produce an emulsion. This emulsion produces selective wetting of the image areas with Shellsol T and the non-image areas with water.

The still wet sheet is now immersed in a bath containing a solution of potassium hydroxide in ethyl alcohol, for example a 10% solution for a period of 20 seconds to decompose the photoconductor in the water containing non-image areas where the decomposing liquid is miscible with the liquid already there, and the sheet is then removed to a water bath or water spray and the coating is washed from the non-image areas. For printing purposes the sheet is then wetted with a wetting agent such as 5% disodium hydrogen phosphate solution in water or a 50% solution of a commercial plate preparation such as "Playtex" and subsequently inked for printing.

On a metal backing the sheet can now be etched selectively and deeply for such applications as printing blocks and also for forming small parts from thin sheet metal.

Example 2.—This can be similar to Example 1 but instead of using an insulating liquid developer (silicone fluid) a concentrated developer is first produced having the following composition:

	Grams
Monolite Red, I.C.I.	100
Lithographic varnish	200
Pentacite P423 gum	100
Cyclohexane	20

The concentrate is mixed in a bar mill to produce a paste. This concentrate is dispersed in Shellsol T or other hydrocarbon solvent having for example a flash point of 135° F. and containing zero aromatics, in the proportions 1 gram of paste to 100 grams of Shellsol T.

This developer is then used as in Example 1 but gives a somewhat more solidly adhering first developer but again having the effect of shielding the image against action by the second liquid.

Example 3.—In Example 1 or 2 an aluminum sheet may be etched after imaging and removal of the coating to etch form a metal part. The etchant can be for example hydrofluoric acid 10%.

Example 4.—In Example 1 or 2 the sheet can comprise a glass backing coated with zinc oxide, bismuth trioxide, lead iodide, cadmium sulphide, cadmium selenide or the like. After removal of the coating from the backing in the non-image area the glass can be etched selectively with hydrofluoric acid.

Example 5.—In Example 1 or 2 a brass sheet can be used and after selective removal of the coating the sheet can be selectively electroplated with gold, chromium, silver, nickel and the like.

Example 6.—The paper, plastic, metal, wood or other sheet can be coated in a vacuum chamber with a thin film of amorphous photoinsulative selenium or sulphur or arsenic trichloride to a thickness of, for example, 0.5 to 5 microns. The sheet is then charged, exposed and developed with a developer of the type shown in Example 1 or 2 modified for example by the substitution of Microlith Black CT for the Monolite Red, and Mineral Turpentine (45% aromatics) for the Shellsol T. The sheet is then selectively wetted in an emulsion having a similar composition to that of Example 1 or 2, modified if desired by the use of Teepol as a surfactant instead of Nonidet.

The plate after selective wetting can be treated to remove the selenium from the non-image areas by the application of a 10% solution of caustic soda NaOH in water or methyl alcohol. The sheet can then be used for similar lithographic or letterpress printing block or transparency purposes.

Example 7.—In Example 6, the selectively dissolved selenium plate can have a glass backing or film base. After removal of the selenium from the non-image areas and selectively from the continuous tones, a transparency having high resolving power results.

Example 8.—In Example 6, the backing can be zinc engraving plate and the final step can be deep etching for letterpress printing.

Example 9.—In Example 6, the backing can be glass and the developer of Example 2 can comprise ceramic powders with flux. Following completion these powders can be fired into the glass by heating in a furnace, for example to 800° C.

Example 10.—The paper, plastic, metal, wood or other sheet can be coated by dip coating or vacuum evaporation or with an organic photoconductor, for example an organic photoconductor coated plate marketed by Kalle A. G. Germany. The sheet is then charged, exposed, and developed with a developer of the type shown in Example 2, modified if desired by the use of Peerless Carbon Black for the Monolite Red, and dispersed in Shellsol T. The emulsion used in Example 2 for selective wetting can be modified if desired by the use of white spirits and water together with a suitable surfactant such as Teepol, or triethanolamine oleate. In the selective removal of the organic photoconductor coating a solution of 5% potassium hydroxide in water is used for a period of 10 seconds to remove the organic photoconductor from the non-image areas. The plate can then be readily used for lithography.

Example 11.—In Example 9, the plate can be aluminum and the end product an etch formed part after etching with hydrofluoric acid, 1 to 10% in water.

Example 12.—In Example 1, 2, 6 or 8, the plate can be a printed circuit laminate and the copper sheet contained thereon can be removed by etching with ferric chloride or acid or the like after selective removal of the photoconductor. Copper conductors can then be formed in the desired areas which retain continuity and edge sharpness in an improved manner.

Example 13.—In Example 1, 2, 6 or 10, the plate can be fabric, cotton, wool, synthetic fibres and the like and the web can be selectively dyed or printed.

It will be seen from these examples that one modification of our process consists of exposing and developing a surface carrying an oleophilic image whilst still wet, selectively wetting said plate with another liquid, then selectively dissolving or decomposing the coating in selected areas to produce a selective resist for subsequent attack or post treatment of the underlying sheet or plate.

Example 14.—In Example 2, in the removal step, there is substituted for the solution of potassium hydroxide in ethyl alcohol, a solution of oleic acid in xylene, which selecting softens the image areas which are water wet. After heating the wetted sheet for 1 minute at 150° F. the softened image areas are removed by wiping with xylene, cumene, mineral turpentine or the like.

Example 15.—In Example 6, where a thin film of amorphous selenium is the photoconductor the potassium hydroxide in ethyl alcohol solution is replaced by a solution of potassium sulphide or sodium sulphide in a higher alcohol or by carbon disulphide.

Example 16.—In Example 10, where the photoconductor film is an organic photoconductor the potassium hydroxide solution is replaced by a solution of benzene or high aromatic solvent.

Example 17.—The zinc oxide-resin coated sheet is

charged, exposed and developed with a developer comprising the following:

	Grams
Water soluble gum (such as starch)	10
Shellsol T, hydrocarbon solvent	50

These compounds are ground together to form a paste and then dispersed in Shellsol T in the proportions 1 gram of paste to 100 grams of Shellsol T. This dispersion is used to develop the image, the gum going down on to the charge retaining area and the hydrocarbon solvent wetting the remaining areas. The sheet is then subjected to water (which forms the second liquid of this process) to remove the water soluble gum and go down in its place, the non-image areas which were wetted with Shellsol T being unaffected by this washing and these areas will resist subsequent acid attack. The water wetted image areas are now subjected to an acid, for example 30% acetic acid which is miscible with the water and decomposes the zinc oxide. The sheet can be inked up selectively and subjected to further decomposition where necessary for example in etching a glass backing.

Example 18. In Example 17, where the photoconductor is zinc oxide, replacing the starch with gum acacia, gum tragacanth, ethyl cellulose and the like.

Example 19.—In example 17, where the photoconductor is replaced by selenium, the gum is replaced by potassium sulphide, this is ground up into a fine powder and dispersed in a similar manner to the gum. Upon wetting with water, the potassium sulphide attacks the selenium and enables its removal.

Example 20.—In Example 17, the photoconductor is replaced by an organic photoconductor such as poly (n-propenylcarbazole) and the gum is replaced by an organic acid such as palmetic acid, lauric acid, myristic acid and the like dispersed in a high boiling point hydrocarbon solvent or in a silicone oil or paraffin oil or the like.

Example 21.—In any of the foregoing examples, the etch solution or the like is replaced by a solution of a ketone such as acetone in water for Example 1 to 10% acetone.

Example 22.—In the foregoing example, the ethyl alcohol or the like is replaced by a solution of an aldehyde in alcohol or water for example a 1% solution.

Example 23.—In the foregoing examples where the coating is resin-bound or is an organic photoconductor the etch solution or the coating is replaced by a solution of chlorothene in alcohol.

What we claim is:

1. A method of conditioning a photoconductor surface comprising the steps of producing an electrostatic latent image on a photoconductor surface on a base, developing the electrostatic latent image by applying to the surface a first developer liquid at least part of which is attractable to the charged areas of the latent electrostatic image, applying to the surface a second liquid which is immiscible with the first liquid, a decomposing agent for the photoconductor surface which is miscible with only one of the said liquids being incorporated into said one liquid for selective decomposition of part of said surface, and then removing the photoconductor surface where decomposed.

2. The method according to claim 1 wherein the first liquid is an electrical insulator and the second liquid is a polar liquid.

3. The method according to claim 1 wherein the first developer liquid comprises an electrically insulating carrier liquid, and carried therein particles which are attractable to the image area and which retain the liquid at the image area.

4. The method according to claim 1 wherein the first developer liquid comprises an electrically insulating liquid and carries therein particles which are attractable to the image area and which retain the liquid at the image area only while the particles remain, said liquid wetting the non-image areas, then with the liquid of the first developer liquid on the non-image areas wetting the image area with said second liquid.

5. The method according to claim 1 comprising the further step of etching the base where the photoconductor is removed.

6. The method according to claim 1 comprising the further step of applying a coating to the base where the photoconductor is removed.

7. The method according to claim 1 wherein the decomposing agent is incorporated into said one liquid before the latter is applied to said surface.

8. The method according to claim 1 wherein the decomposing agent is incorporated into said one liquid after the latter is applied to said surface.

9. The method according to claim 1 wherein the decomposing agent is selected from the group consisting of potassium hydroxide, sodium sulphide and sodium hydroxide in solution.

10. The method according to claim 9 wherein the surface is selected from the group consisting of zinc oxide and selenium.

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