Contact Transfer Electrostatic Copying Apparatus

Inventors: Ian Edward Smith, Lockleys; Peter John Hastwell, Elizabeth Grove; Marinus Cornelius Vermeulen, Valley View, all of Australia

Assignee: Savin Business Machines Corporation, Valhalla, N.Y.

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Primary Examiner—Robert P. Greiner
Attorney, Agent, or Firm—Shenier & O'Connor

ABSTRACT

An electrophotographic copying machine employs a method of contact transfer of developed electrostatic images. A moving photoconductive surface is charged and exposed to a pattern of light and shade as done in known electrophotographic processes, and the latent image is developed with a liquid developer which carries a toner which is tacky-that is, one that has adhesive properties. The developed image with the toner in tacky state is contacted with sheet material such as paper, which has greater affinity for the tacky toner than the photoconductive surface from which the image is transferred. After the image is transferred to the sheet material the toner quickly loses its tackiness and dries to a hard scuff-resistant surface. Transfer of the tacky toner may be facilitated by heating the sheet material before contact is made between it and the developed image.

7 Claims, 6 Drawing Figures
CONTACT TRANSFER ELECTROSTATIC COPYING APPARATUS

This is a division of application Ser. No. 155,108, filed June 21, 1971.

BACKGROUND OF THE INVENTION

Electrostatic reproduction processes are well known to the art. In the well-known Xerox system a photoconductive surface carried by a drum is electrostatically charged by a corona discharge device. The photoconductive surface which may be of selenium or the like is an insulator in the drak and a conductor in the light. The image to be reproduced is focused on the photoconductive surface. When the light strikes the photoconductive surface the charge leaks away in the illuminated areas leaving the dark areas to form the image. The latent image in the form of electrostatic charges on the photoconductive surface is then developed by a toner. This toner must be in the form of a dry powder. The dry toner particles are then transferred by an electrostatic charge to sheet material such as ordinary paper and are usually formed from thermoplastic resins. The toner particles are then fixed by heat on the ordinary paper and the image appears in its final form. The necessity of using heat to fix the toner particles prevents high-speed operation of the Xerox system. Furthermore, the dry toners are slightly abrasive and sooner or later they scratch and mar the selenium surface of the drum which is the heart of the Xerox machine. The dry toner also causes mechanical problems since the toner particles become airborne and permeate the bearings of the machine. This requires frequent cleaning, which is an onerous task. The dry toners have inherent dielectrophoretic properties which prevent their filling in large black areas. This is easily observed by viewing any copy which has a large, black area made on the Xerox machine.

In the Electrafax method, a sheet of paper is covered with a photoconductive such as zinc oxide. The latent electrostatic image can be developed either by a dry toner or by a liquid in which a toner is suspended. A liquid developer comprises finely divided pigment particles having an average size no larger than about twenty microns and probably much smaller to about an average size of about five microns, suspended in a relatively non-conductive light hydrocarbon such as benzene, toluene, hexane, naphtha, cyclohexane, or the like. The final image, of course, in the Electrofax process, appears on the photoconductor-coated surface and is not transferred to ordinary paper. It has been realized for some time by those skilled in the art that it would be desirable to use liquid developers in a transfer process. No one has found a way, however, to accomplish this conveniently. In U.S. Pat. No. 3,251,688 issued May 17, 1966, to Mihajlov, one attempt at the employment of liquid developers in a transfer process is shown. Mihajlov applies a film of liquid developer over the photoconductive surface. He then exposes the photoconductive surface and the developer simultaneously to a pattern of light and shadow. He then attempts to transfer the image to an ordinary paper. He has found, however, that the non-image areas have background toner. He attempts to reduce this by applying an electrical potential of the same polarity as that of the toner to the roll which presses the paper against the film of developer and makes the roller of conductive rubber or the like.

In all of the processes of the prior art in which transfer of an image is made from a photoconductor to ordinary paper, there is a loss of definition according to the application of pressure which distorts the developed image or through the difficulty of attaining effective transfer of development particles to a new location and the effective fixing of the same. Difficulty is also experienced when the same photoconductive surface is used repetitively, and images produced on it successively are transferred to another medium. The problem is that the photoconductive surface becomes soiled. This soiling is not very great when dry toners are used but in a method such as that of Mihajlov, the liquid toner will adhere to some extent to the photoconductive surface and gradually become unusable.

SUMMARY OF THE INVENTION

One object of our invention is to provide a novel method of contact transfer of developed electrostatic images from the surface of a photoconductor to sheet material such as paper.

Another object of our invention is to provide a novel method of contact transfer of electrostatic images developed by a liquid developer to ordinary paper or the like.

Another object of our invention is to provide a novel method of contact transfer of a liquid toner developed electrostatic image from the photoconductive surface in an expedient and simple manner without the use of an electrostatic field.

Still another object of our invention is to provide a method of contact transfer of liquid toner developed electrostatic images while maintaining high resolution.

A further object of our invention is to provide a method of contact transfer of a liquid toner developed electrostatic image from a photoconductive surface to a copy sheet while maintaining the photoconductive surface in a clean condition.

Another object of our invention is to provide a photoconductive surface having less affinity for the developed electrostatic image than for the paper to which it is to be transferred.

Another object of our invention is to provide an improved liquid toner or developer which can readily be applied to a latent electrostatic image on a photoconductive surface from which it can readily be transferred to a second surface such as ordinary paper or the like.

A further object of our invention is to provide a novel liquid toner or developer which is non-sticky when first deposited, becomes sticky or tacky after deposit so it can be transferred while tacky and loses its tackiness and remains firmly bonded to the surface to which it is transferred.

Another object of our invention is to provide a toner which can be transferred while tacky to a dry surface and then cured to provide a scuff-free and abrasion-resistant final image.

Still another object of our invention is to provide a developer or toner which when tacky will have greater affinity for paper than the photoconductive surface on which the image was developed.

A further object of our invention is to provide novel apparatus for carrying out our novel method.
A further object of our invention is to provide a novel sheet material having affinity for a tacky toner developed image. Other and further objects of our invention will appear in the following description.

In general, our invention contemplates the provision of a photoconductive surface which may be carried by a drum or moving belt or the like. The surface, is adapted to be charged electrostatically by a corona discharge device which is well known in the art. The original which is to be copied or reproduced is projected upon the charged surface. Where light strikes, the charge is conducted to ground through the photoconductor leaving a pattern of charges such as electrons faithfully reproducing the image in a latent fashion. The latent image is then developed with a liquid toner having transient adhesive or tacky properties. The toner composition has low adhesion for the image-forming surface and high-adhesion for the copy surface. The tacky or adhesive properties are transient and the final image exhibits high resolution and is scuff-free. While our invention contemplates the use of ordinary paper, other appropriate sheet material such as thin sheets of plastic, aluminum foil or the like may be used if desired. The copy paper may be coated with a thin film of synthetic resin for which the toner particles suspended in the developer liquid have affinity. This procedure will permit a wider variety of developer liquids to be used. This eliminates the criticality or close limits of components in the confection of the developer liquids.

BRIEF DESCRIPTION OF THE DRAWINGS

In the accompanying drawings which form part of the instant specification and which are to be read in conjunction therewith and in which like reference numerals are used to indicate like parts of the various views:

FIG. 1 is a diagrammatic sectional view of a photocopier adapted to carry out the method of our invention and embodying one form of the apparatus of our invention.

FIG. 2 is a diagrammatic view showing the driving train for the photocopier shown in FIG. 1.

FIG. 3 is a diagrammatic view showing the driving train for the photocopier shown in FIG. 1.

FIG. 4 is a diagrammatic sectional view similar to that shown in FIG. 1 showing another embodiment of apparatus involving our invention and capable of carrying out the process of our invention.

FIG. 5 is a diagrammatic view similar to that shown in FIG. 1 of apparatus adapted to make a printing roller by the process of our invention.

FIG. 6 is a diagrammatic view showing the printing roller made by the apparatus shown in FIG. 5 assembled in a machine for making Xerographic prints in rapid succession.

DESCRIPTION OF THE PREFERRED EMBODIMENT

More particularly referring now to the drawings, in FIG. 1 the photocopier indicated generally by the reference numeral 10 comprises a light-tight housing 12 in which we position a rotary drum 14 bearing a photoconductive layer 16. Drum 14 is made of conductive material and carries a photoconductive layer 16 we will describe in greater detail hereinafter. Mounted on top of the housing 12 is a carriage 18 adapted to reciprocate on suitable bearings 20. The carriage 18 supports a transparent plate 22 on which an original 24 to be copied is mounted. The reciprocating carrier 18 is adapted to move the original back and forth past the light 26 (also identified as L1) which illuminates the copy. The movement of the carriage 18 is synchronized with the rotation of the drum 14 such that the peripheral speed of the drum and the linear motion of the carriage 18 are identical. As copy passes by the lens 28 the image is focused upon the surface of the photoconductive layer 16. A mirror 30 which may be a prism if desired directs the image at right angles to the surface of the photoconductive layer 16. The limits of the path of travel of the carriage are determined by limit switch LS1 in the direction to the right as viewed in FIG. 1 and limit switch LS2 as viewed to the left in FIG. 1. It is understood, of course, that switch LS2 is positioned much further to the left, a part of the support being shown broken away because of space limitations on the drawing. Drum 14 is mounted on the shaft 32 and its surface is in contact with rollers 33, 34, and 35, which are positioned in a tank 36 containing the developer liquid 38 of our invention.

A motor M2 is adapted to drive an agitator 40 to keep the developer liquid agitated so that the insoluble components of the developer will remain dispersed throughout the developer liquid. A shaft 42 carries roll of paper 44 or other flexible sheet material to which the copy is to be transferred. A motor M3 drives a centrifugal fan 46 to furnish air to an elongated nozzle 48 adjacent the periphery of the drum 14 to remove excess developer liquid from the surface 16 of the drum. A plurality of hot air manifolds 50, 52, 54 and 56 are controlled by respective valves connected to a supply of hot air (not shown). Hot air from manifold 50 is directed against the surface 16 of the periphery drum 14. Manifold 52 directs hot air to the side of the paper which is to receive the transfer from the drum. Manifold 54 directs hot air on the opposite side of the paper. Manifold 56 directs hot air to the finished transfer after it has been severed from the roll by knife 60 operated by solenoid 52. Paper is drawn from the roll 44 by takeoff roller 62 and the cut sheet is then moved by delivery roll 64. As will be pointed out hereinafter the positions of the respective valves controlling the hot air may be varied depending upon the particular composition of the developing liquid being used. The use of hot air manifolds are beneficial but not absolutely essential for the practicing of our method. They are particularly useful where high-speed operation and a rapid reproduction rate is desired. A corona discharge device 66 (K) is positioned adjacent the photoconductor surface of the drum to charge its surface in the dark. A cleaning roller 68, which may be wet if desired, removes any residual toner which may be inadvertently left on the surface of the drum.

Shielded light 70 (L2) insures that a residual electrostatic charge is conducted to ground before the surface of the drum is recharged.

Referring now to FIG. 2 the moving parts of our photocopier are driven from a prime mover to be indicated by the reference numeral 100 and a motor M1. The motor 100 drives a shaft 32 which carries for rotation therewith, a first-gear wheel 102, a second-gear wheel 104 and a pinion 106. A shaft 31 carries a pinion 108 for rotation therewith. A pinion 110 which is loosely
mounted on shaft 31 engages a rack 112 which is carried by and secured to the carriage 18. A clutch C1 is secured to shaft 31 for rotation therewith. A pinion 114 is mounted on a side shaft 39 for rotation therewith. Pinion 107 is driven by shaft 31 and drives pinion 109 which drives pinion 111 to drive shaft 39. Pinion 114 is in engagement with the pinion 116 which is mounted for rotation with shaft 29 which shaft carries a clutch C2. It will be seen clutch C1 rotates in one direction and clutch C2 rotates in the opposite direction. When clutch C1 is energized it will engage the loosely mounted pinion 110 and drive the rack 112 in one direction. When clutch C2 is energized it will engage the pinion 110 and drive the rack 112 in the opposite direction. The pinion 108 is driven from the gear 102 to gear chain 120. The pinion 106 drives the pinion 122 through a gear chain 124. This drives the roller 34. Rollers 33 and 35 are driven through intermediate gears 123, 124, 125, 126 and 127. The developer applying rollers 33, 34 and 35 rotate in the same direction. The ratio of the gear chain and pinions is such that peripheral speed of the rollers 33, 34 and 35 is the same as the peripheral speed of the drum 16. A takeoff roller 62 is mounted on a shaft 61 for rotation therewith. A clutch C3 is mounted on the shaft 61 for rotation therewith. The shaft 61 carries a pinion 128 loosely so that the pinion may rotate freely. The pinion 128 is driven by gear chain 130 from the gear wheel 104. When the clutch C3 is energized the takeoff roller will rotate. A pinion 132 is driven from the pinion 128 by a gear chain 134. It rotates continuously and is mounted on the shaft 63 which carries the delivery roller 64.

Referring again to FIG. 1 the paper on which copy is to be made passes from the roll 44 over printing roller 43 mounted on a shaft 41. The shaft is carried by a pair of links 45 pivotally mounted on a shaft 47. When the arcuate solenoid S1 is energized the links move downwardly to bring the paper into contact with the rotary drum to effect the transfer of the developed image to the paper.

Referring now to FIG. 3, which shows the control circuit for our copier, at the start of an operation limit switches LS1 and LS2 are in the positions shown in the drawing. The carriage 18 is to the right as viewed in FIG. 1. An original sheet to be copied is placed upon the transparent plate 22. The machine is energized by closing switch TS. The main lines 200 and 202 are connected across an appropriate source of potential. The closing of the switch TS energizes the main motor M1, the blower motor M3 and the agitator motor M2. It also energizes the erasing light L2. To start the operation of the copier, push button PB is pressed just momentarily. This completes a circuit through the relay winding 1R and closes normally open relay contacts 1R1, 1R2 and 1R3. The contact 1R1 completes a holding circuit through LS2 and maintains the relay winding 1R in energized condition. The circuit through contacts 1R2 energizes clutch C1 and drives the carriage to the left as viewed in FIG. 1. The circuit through contacts 1R3 energizes the light L1 and the corona discharge device K. The original passes by the light and an image of it is focused upon the moving drum by the lens 28 and the mirror or prism 30. A latent image electron image is impressed upon the photoconductive surface 16 as is known in the art. This latent image is later developed by the developing liquid owing to the movement of adhesive toner particles suspended in the developing liquid to the charged portions of the drum. The air knife blows excess developing liquid from the drum. As the carriage 18 moves to the left it strikes limit switch LS2. This switch now moves downwardly from the position shown in FIG. 3 to break the holding circuit through 1R1 and thus opens the circuits through 1R2 and 1R3. The opening of the circuit through 1R2 de-energizes clutch C1. The opening of the circuit through 1R3 de-energizes the corona charging circuit K and de-energizes the illuminating lamp L1. A circuit is now made through winding 2R. The energization for winding 2R closes circuit through 2R1, 2R2, 2R3 and 2R4. The closing of the circuit through 2R1 completes a holding circuit and maintains the winding 2R energized, the circuit now being completed from main 200 through winding 2R through contacts 2R1 through normally closed contacts 3R1 to the other side of the line 202. The closing of contacts 2R2 energizes clutch C2 through normally closed (in the position shown) limit switch LS1 and drives the carriage 18 in the reverse direction. The closing of contacts 2R3 energizes solenoid S1 to draw the printing roller 43 downwardly against the action of the spring 49. The tacky toned image is then transferred to the paper. The clutch C3 is also energized so the take-off roller 62 will rotate to draw the paper from the roll and pass it to the right through the delivery rollers 64. As can be seen by reference to FIG. 1 both the rollers 62 and 64 have backup rollers against which they bear. The closing of contacts 2R4 partially completes a circuit through winding 3R. When the carriage on its return to the right strikes limit switch LS1 it moves it from its normal position shown in FIG. 3 upwardly. This completes a circuit through winding 3R. Energization of winding 3R closes the contacts through 3R2 and energizes solenoid S2 which operates the cutting knife 60. It also breaks the holding circuit through winding 2R. This permits contacts 2R1, 2R2, 2R3 and 2R4 to reassume their open positions. When contacts 2R4 are broken the relay winding 3R is de-energized and contacts 3R2 are opened to de-energize winding of solenoid S2. It will be understood, that while we have described the cycle for a single operation, successive cycles to any desired number may be initiated by a sequenc means known to the art, whereby the cycle will be repeated as desired to make multiple copies automatically. This can be easily accomplished by having a sequencing switch act to close the circuit through PB completed by a synchronous brush instead of by a push button. It is to be understood, of course, that the limit switches are biased by the appropriate means such as springs to assume the positions shown in FIG. 3 at the end of a cycle of operations.

Referring now to FIG. 4, we have shown a modified form of the machine shown in FIG. 1. Instead of a drum carrying a photoconductive layer we provide a belt 300 having a photoconductive layer 16. The belt is pressed around a pair of conductive drums 302 and 304. The sheet material to which the image is to be transferred passes from roll 44 over guide roll 306 under guide roll 308 around the belt 300 carrying the photoconductive layer 16 and then over guide roll 310 to takeoff roller 62.

In the form of the invention shown in FIG. 4 an elongated manifold 53 heats the rear side of the copy paper by hot air delivered to the manifold and controlled by a valve. The cleaning roll in the form of the invention shown in FIG. 4 is disposed in a tank 69 containing
cleaning fluid 71 so that the cleaning roll 68 may remove residual toner which may inadvertently or accidentally adhere to the photoconductive surface of the belt.

The belt may be made of any appropriate material which is flexible and conductive such as wire mesh, fibers of synthetic resin impregnated with conductive material and woven into a belt, or flexible metallic screen, or the like. The photoconductive layer will be described more fully hereinafter. It will be recognized that the arrangement shown in FIG. 4 is essentially the same as that shown in FIG. 1, except that a belt is used instead of a drum. Since the imaging station is removed from the transfer station, it is not necessary to use a solenoid 51 to bring the copy paper into contact with the drum.

Referring now to FIG. 5, the arrangement is quite similar to that shown in FIG. 1, except that instead of transferring a toned image from the photoconductive layer 16 to sheet material, the transfer is made onto a conductive drum 400 mounted on a shaft 402. The transferred image indicated at 403 is fixed by a radiant heater 404.

Referring now to FIG. 6, the drum 400 having the image 403 thereon is mounted on a shaft 406. The toner-formed image 403 is non-conductive so that when it is charged by the corona discharge from corona discharge device 60 only the image will retain the charge. The charge elsewhere on drum 400 will be conducted to ground so that it is conductive. Accordingly, when the charged image is subjected to the developer solution as fed by the rolls 33, 34 and 35 from the toner liquid in the tank 36, the drum will act as a printing drum and transfer the freshly toned portion of the image 403 on the paper drawn from the roll 44. It will be observed that this operation may take place in broad daylight since no photoconductive phenomenon is involved. The charge is retained on the non-conductive image formed by the toner particles and the charge upon the image will pick up toner and transfer the toner image to a portion of the roll of paper or other sheet materials. It is to be understood, of course, that the printing drum 400 may be provided with a cleaning roller 68.

The developer according to the present invention is so arranged that it is more adhesive in respect of the surface to which it is to be transferred than it is to the surface on which the latent image is produced. Accordingly, when the latent image is developed it can readily be transferred to the copy sheet because of its greater affinity for it.

In its simplest aspect we may give the photoconductive surface low adhesion by treating the same to provide a silicone or a urethane film. Similarly it is feasible to treat paper with a medium which will give the paper a physical affinity for the toner, that is, the developed toner image. In a similar manner it is possible to cool the photoconductive surface and heat the copy paper. This temperature differential will have the effect of enhancing the affinity of the developed image with a copy paper.

To make a photoconductive surface for the drum 14 or the conductive belt 300 which will have a low affinity for the developed image we proceed in a number of different ways to accomplish this result.

EXAMPLE 1

Prepare a mixture as follows:

Dyes may be added to the above mixture, as is well known in the art, to obtain the required photosensitivity. This mixture is then ballmilled for 12 hours. It is then diluted with the following solution:

This mixture is then applied to the drum or the belt and cured. After curing, a thin film of an emulsion of a silicone resin together with an appropriate catalyst such as lead monoxide, benzoyl peroxide or the like, is mixed in a light hydrocarbon (boiling range 60° C - 140° C) and is applied over the photoconductive surface. The catalyst is used to the extent of 10 percent of the resin and the film concentration is coated at 8 percent. The film is then cured from 4 to 6 hours at 150° C or 16 to 32 hours at 71° C. Tests made on a photoconductive surface as described in this example enabled a total of 800 images to be developed on 6 feet of belt and transferred to copy paper at the rate of 42 feet per minute.

EXAMPLE 2

Prepare a mixture as follows:
instead of being applied on the surface. This produces a photoconductive layer which has low adhesive properties. This mixture is then coated on a suitable substrate such as a conductive drum or belt and cured to form the photoconductive surface.

**EXAMPLE 3**

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Component</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 gms.</td>
<td>Zinc Oxide</td>
</tr>
<tr>
<td>27 gms.</td>
<td>short oil (safflower)</td>
</tr>
<tr>
<td>20 gms.</td>
<td>oxidizing alkyd resin</td>
</tr>
<tr>
<td></td>
<td>an emulsion of silicone</td>
</tr>
<tr>
<td></td>
<td>resin ballmilled with an</td>
</tr>
<tr>
<td></td>
<td>appropriate catalyst such</td>
</tr>
<tr>
<td></td>
<td>as lead monoxide, benzoxy</td>
</tr>
<tr>
<td></td>
<td>peroxide, or the like.</td>
</tr>
<tr>
<td>10 mls.</td>
<td>hydrocarbon solvent having</td>
</tr>
<tr>
<td></td>
<td>a boiling range between</td>
</tr>
<tr>
<td></td>
<td>100°C and 120°C.</td>
</tr>
<tr>
<td>10 mls.</td>
<td>Terpineol</td>
</tr>
</tbody>
</table>

The above mixture is then ballmilled with dyes to obtain the required photosensitivity as is known in the art and diluted with:

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Component</th>
</tr>
</thead>
<tbody>
<tr>
<td>40 mls.</td>
<td>hydrocarbon solvent having a</td>
</tr>
<tr>
<td></td>
<td>boiling range between 100°C and</td>
</tr>
<tr>
<td></td>
<td>120°C.</td>
</tr>
<tr>
<td>10 mls.</td>
<td>Toluol</td>
</tr>
<tr>
<td>10 mls.</td>
<td>Terpineol</td>
</tr>
<tr>
<td>0.2 gms.</td>
<td>Cobalt Naphthenate used</td>
</tr>
<tr>
<td>0.5 gms.</td>
<td>Lead Naphthenate as</td>
</tr>
<tr>
<td>1.6 gms.</td>
<td>Zirconium Octoate dryers</td>
</tr>
</tbody>
</table>

This mixture is then applied to a substrate and cured.

**EXAMPLE 4**

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Component</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,000 gms.</td>
<td>Zinc Oxide</td>
</tr>
<tr>
<td>415 gms.</td>
<td>Polyurethane Alkyd Resin</td>
</tr>
<tr>
<td>400 mls.</td>
<td>hydrocarbon solvent having</td>
</tr>
<tr>
<td></td>
<td>a boiling range between</td>
</tr>
<tr>
<td></td>
<td>100°C and 120°C.</td>
</tr>
</tbody>
</table>

Dyes are added to obtain the required photosensitivity and the mixture is then ballmilled as in **EXAMPLE 1**. It is then diluted with:

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Component</th>
</tr>
</thead>
<tbody>
<tr>
<td>300 mls.</td>
<td>Toluene</td>
</tr>
<tr>
<td>300 mls.</td>
<td>hydrocarbon solvent having a boiling range between 100°C and 120°C.</td>
</tr>
<tr>
<td>300 mls.</td>
<td>Chloroethylene</td>
</tr>
<tr>
<td>3 gms.</td>
<td>suitable dryers such as Cobalt Naphthenate, Lead Naphthenate and Zirconium Octoate.</td>
</tr>
</tbody>
</table>

The mixture is then coated on the substrate and cured as before.

It will be observed that in the above examples the photoconductive material which is coated on the drum or the belt substrate is compounded so that the photoconductive layer will have a reduced adhesion for the tacky toner.

Ordinarily, it is more desirable to be able to employ untreated paper as the copy sheet to which the tacky toned image is to be transferred. However, it is also contemplated by our invention that a paper treated to have special affinity for the tacky toner can be employed. For example, we have treated the paper with a solution of an acid maleic-modified vinyl chloride and vinyl acetate copolymer. The solvent is evaporated and it will be found that the paper thus treated has a special affinity for the tacky toned image.

Another example of a coating for paper is a solution of a vinyl-toluene butadiene copolymer resin. These resins are available from the Goodyear Tire and Rubber Company and sold under the trademark "PLIOLITE." They are soluble and aliphatic solvents and films are formed by simple evaporation of the solvents. A paper coated with "PLIOLITE" resin exhibits affinity for the tacky toned image. Another example of a coated paper is one coated with a solution of polyvinyl butyral. This synthetic resin is dissolved in alcohol to form a 4% solution. It is then applied to the paper to form a thin continuous film. The affinity for the toner in each case of the paper coated with the examples given above was such that transfer took place from the photoconductive layer to the paper. It is of interest to note that the pressure to effect the transfer is very slight. As a matter of fact if too much pressure is used it was found that the transfer of the toned image from the photoconductor to the paper was less effective.

It is not necessary that the developer deposit a toner in a tacky or sticky condition. The developer may be such that the toned image is non-tacky at first then becomes tacky or adhesive so it can be transferred in a tacky state and then as the solvent evaporates, dries or cures and loses its stickiness and remains firmly bonded to the surface to which it was transferred.

According to our invention the adhesive toner comprises a relatively large amount of a high molecular weight polymer adapted to form a continuous pigmented polymer matrix exhibiting high cohesion and tackiness. In general, high molecular weight polymers are dissolved in a suitable solvent. The solution of the high molecular weight polymer is pigmented with a suitable pigment such as microlith black and the solution suspended in a low power solvent or diluent with the aid of a dispersing agent. The high molecular weight polymer may be one which has a low adhesion for the image forming surface and a high affinity for the copy surface. Alternatively the high molecular weight polymer may have low adhesion for both surfaces and a tackifier is combined with the polymer to create the high adhesion for the copy paper. The main characteristic of the high molecular weight polymer, however, is that it is generally insoluble in the diluent which we employ in making our developer fluid. The diluent which we prefer is that manufactured by the Standard Oil Company of New Jersey and sold under the trademark "ISOPAR G." This is an isomerized paraffinic hydrocarbon having a specific gravity of .75 at 60°F. This product is substantially 100 percent pure isoparaffin. It has a boiling range from 57° C to 77° C. "ISOPAR H" is a similar product and has a boiling range from 177° C to 188° C. This is disadvantageous in that it takes a longer period of time for the copies to dry. The feature which characterizes the diluent is that it has low solubility for the solution of the high molecular weight polymer which is suspended throughout the diluent by a suitable dispersing agent. "ISOPAR G" has a kauri butanol number of 27. This is true of "ISOPAR E" which has an initial boiling point of 116° C and a final boiling point of 143° C. "ISOPAR E", however, is dangerous to use since it has a flash point of 50° F. The flash point of "ISOPAR G" is 105° F, and it is therefore a safe diluent. Because the tacky toner particles must migrate through the diluent under the influence of an
11 electrostatic charge, the diluent must possess a low surface tension. "ISOPAR" is low in surface tension and high in interfacial tension. This accounts for its excellent demulsibility. Though other diluents which have low solvent power for the tacky toner organosol can be used, we prefer "ISOPAR" because of its manifold advantages in our process.

High molecular weight polymers which are used to form the solution to which the toner component is added are such that they are not soluble in the diluent. Appropriate high molecular weight resins which can be used are as follows:

<table>
<thead>
<tr>
<th>High Molecular Weight Resins</th>
<th>Manufacturer</th>
<th>Trademark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vinyl-toluene/acylate copolymer*</td>
<td>Goodyear Tire &amp; Rubber Co., Akron, Ohio</td>
<td>&quot;PLIOLITE VTAC&quot;</td>
</tr>
<tr>
<td>Styrene/acylate copolymer*</td>
<td>Goodyear Tire &amp; Rubber Co.</td>
<td>&quot;PLIOLITE AC&quot;</td>
</tr>
<tr>
<td>Styrene copolymer</td>
<td>Goodyear Tire &amp; Rubber Co.</td>
<td>&quot;PLIOLITE S-5A&quot;</td>
</tr>
<tr>
<td>Butadiene-styrene copolymer**</td>
<td>Phillips Petroleum Co.</td>
<td>&quot;SOLPREENE&quot;</td>
</tr>
</tbody>
</table>

* Solutions of this resin in solvents having kaurn-butanol values of 36 and higher dry rapidly to form tough, hard films with good adhesion. Furthermore, a solution of this resin will not dissolve in "ISOPAR G" (which is one of our diluents) which has a kaurn-butanol number of 27.

** "SOLPREENE 303" is a solution-polymerized copolymer in the ratio of 52/48 with partial block distribution of the styrene along the molecular chain. "SOLPREENE 1205" is a copolymer of butadiene and styrene in the ratio of 75/25 manufactured by the solution polymerization process.

These resins are readily soluble in hydrocarbon solvents having high kaurn-butanol numbers of 50 or more. An appropriate solvent is the hydrocarbon solvent manufactured by Standard Oil Company of New Jersey and sold under the trademark "SOLVESSO 100." It has an initial boiling point of 159°C and a final boiling point or end point of 182°C. It consists largely of aromatic hydrocarbons and has a kaurn-butanol number of 91. It is to be understood that any appropriate solvent may be employed. However, since some of the solvent for the resin will be present in the developer solution, its end point should be low.

As is pointed out above, "ISOPAR G" has an end point of 177°C. "SOLVESSO 100" has an end point of 182°C. "SOLVESSO 150" could be used, if desired, but it has an end point of 212°C. The particular solvent is not critical as long as it is a solvent for the high molecular weight resin and can be evaporated at convenient temperatures from the final developer solution.

While the high molecular weight resins we employ exhibit tackiness upon drying, that is, when they are almost dry, it is desirable to increase the tackiness. This is done by adding a resin which has tacky properties to the solution of the high molecular polymer. The resin which is added for tackiness, as is the case with high molecular weight resins, must be soluble in the solvent for the high molecular weight resin and substantially insoluble in the diluent which is being used for the developer liquid.

We have found that appropriate tackifier resins are as follows:

<table>
<thead>
<tr>
<th>Tackifier Resins</th>
<th>Manufacturer</th>
<th>Trademark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymerized alpha pinene</td>
<td>Pennsylvania Industrial</td>
<td>&quot;PICCOLYTE ALPHA&quot;</td>
</tr>
</tbody>
</table>

12 The high molecular weight resins may be plasticized to render them tacky by modifying agents. These are:

<table>
<thead>
<tr>
<th>Plasticizers for High Molecular Weight Resins</th>
<th>Manufacturer</th>
<th>Trademark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dibutyl phthalate</td>
<td>Celanese Corp. of America</td>
<td></td>
</tr>
<tr>
<td>Dioctyl phthalate</td>
<td>Celanese Corp. of America</td>
<td></td>
</tr>
<tr>
<td>Dimethyl phthalate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Di-2-ethyl phthalate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Di-2-isobutyl phthalate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chlorinated polyphenylate</td>
<td>Monsanto Chemical Company</td>
<td>&quot;AROCLOL 1254&quot;</td>
</tr>
<tr>
<td>Tricresyl phosphate</td>
<td>Union Carbide Plastics Co.</td>
<td></td>
</tr>
</tbody>
</table>

Some of the high molecular weight resins, such as "PLIOLITE VTAC," do not possess sufficient tackiness to effect complete transfer. We have seen that a tackifier resin may be added compatible with the high molecular weight resin to give the organosol the desired tackiness. This tackiness can be achieved by adding plasticizers to the high molecular weight resin. These plasticizers have the property of imparting tackiness to the high molecular weight resin so that less or no tackifier resin may be employed.

In carrying out our invention, we first manufacture the organosol by dissolving a high molecular weight resin or a mixture of high molecular weight resins in an appropriate solvent.

**EXAMPLE A**

The following formulation is prepared:

37.5 gms. "PLIOLITE VTAC"
40.0 gms. "SOLPREENE 1205"
100.0 gms. "SOLVESSO 100"

As we have pointed out above, "SOLVESSO 100" is an ideal solvent. Any other appropriate solvent such as terpineol can be employed. The above formulation is emulsified in a high-speed emulsifying mill, together
with 1100 mls. of a diluent such as "ISOPAR G." A quantity of this organosol is further diluted with "ISOPAR G" to any desired extent to form a suspension. This suspension produces a tacky resin deposit on a negative polarity electrostatic surface charge.

The toner component is formulated to be compatible with the resin organosol, since it must be physically attached to the resin developer aggregates or co-deposit at a rate in substantially the same proportion as the ratio of toner component to the organosol solids. If the toner component is not compatible with the organosol solution, it will act as a separate system and deposit at a greater rate than the organosol. This will pull the pigment out of the developer liquid, and the deposit will be predominantly pigment. This will result in low cohesion and poor transfer qualities.

The toner should have the same resin system as the organosol. In the example we are considering, the two resins used were "PLIOLITE VTAC" and SOLPRENE 1205." The pigment may be of any desired nature, as for example, carbon black, having a particle size on the average of 25 millimicrons. Any desired pigment may be used as, for example, reflex blue pigment with the carbon black. The pigment is advantageously coated with a modifying resin or a drying oil. A toner matching the organosol of this Example A is as follows:

100.0 gms. microlith black
12.5 gms. reflex blue
25.0 gms. "PLIOLITE VTAC"
25.0 gms. "SOLPRENE 1205"

Sufficient toluol was added to the above mixture to achieve the correct milling viscosity for milling in a tri-ple-roll mill. After milling, the mixture was diluted with 600 mls. of "ISOPAR G." This toner is effective for negatively charged electrophotographic images.

The resin organosol and the toner component are mixed in a high-speed emulsifying mill and the constituents milled together. The resin solution prepared as described above was diluted with 1100 mls. of "ISOPAR G" and milled for one minute. Then 120 mls. of the toner component were added and the mixture milled for three additional minutes. This concentrated adhesive toner was further diluted in a ratio of 50 mls. of toner to 200 mls. of "ISOPAR G" to produce a developer liquid. Adhesive or tacky toner in this developer liquid is readily deposited on a negative polarity surface charge. It will be understood that there is nothing critical in the method of mixing the components. The toner components may first be added to the mill with 1100 mls. of "ISOPAR G" and then followed by mixing with the resin solution. Alternatively, the resin and the toner may be combined and then added to the mill with the diluent.

This adhesive toner developing liquid produced good image transfer between an organic photoconductor and an uncoated paper such as Velvet Book Opaque. It also produced good transfer between a zinc oxide resin photoconductor and a Velvet Book Opaque paper. A low density image was observed on the zinc oxide photoconductor after transfer. The photoconductive surface was a commercial zinc oxide photoconductor and not one of our special non-adhesive formulations as described above.

We then formulated another organosol component as follows:

\[
\begin{align*}
37.5 \text{ gms.} & \quad "PLIOLITE VTAC" \\
20.0 \text{ gms.} & \quad "BETAPRENE BC 100" \text{ which is a tackifier resin} \\
100.0 \text{ gms.} & \quad "SOLVESO 100" \\
\end{align*}
\]

The addition of the tackifier to the resin component and its incorporation into the developing fluid in the manner identical to that described above produced a developing fluid in which the image transfer from the organic photoconductor to the Velvet Book paper was less complete. On the other hand, when this toner was used with art paper, the transfer was more complete. It is to be understood, of course, that the photoconductors tested were not of the type of our invention having a low adhesion. When these toners were tested with photoconductors of our invention, the transfer of our tacky toner from the photoconductive surface to the paper was substantially complete.

The amount of toner component combined with the organosol component changes the adhesive properties. With 120 mls. of toner component, optimum adhesive transfer properties were achieved. The toner component in the amount of 60 mls. produced a deposit of low optical density and there was greater sedimentation of the toner concentrate. A toner component of 240 mls. produced an optically dense deposit. The cohesion and adhesion were lowered with a resultant loss of transfer properties.

\[
\begin{align*}
37.5 \text{ gms.} & \quad "SOLPRENE 303" \\
20.0 \text{ gms.} & \quad "PICCOLYTE ALPHA" \\
10.0 \text{ gms.} & \quad \text{Polystyrene (melting point } 75°C, \text{ approximate molecular weight } 400\) \}
\]

This resin mixture is milled in a high-speed emulsifying mill together with 1100 mls. of a diluent such as "ISOPAR G." This forms the resin solution or organosol.

The toner component matching the Example C organosol was made as follows:

\[
\begin{align*}
200 \text{ gms.} & \quad \text{microlith black} \\
25 \text{ gms.} & \quad \text{reflex blue} \\
50 \text{ gms.} & \quad "PLIOLITE S-SD" \\
75 \text{ gms.} & \quad "SOLPRENE 1205" \\
\end{align*}
\]

These were placed in a triple-roll mill and sufficient toluol was added to dissolve the mix and produce good milling viscosity. The mix was then diluted with 1200 mls. of "ISOPAR G" in a high-speed emulsifying mill. The resin mix was added to 1100 mls. of "ISOPAR G" in a high-speed emulsifying mill, to which was then added 120 mls. of the toner component Type C. This produced a developing liquid of our invention which exhibited low adhesion for both the organic and zinc oxide photoconductors and high adhesion for bond paper, Velvet Book paper, and art paper.

It will be observed that in each case the toner component is compatible with the organosol, so that the high molecular weight polymer nucleates or attaches to the toner component. In order to achieve this, the pigment must be wetted with a material which allows compatibility with the high molecular weight polymer. After the toner component is milled, it is tested for its elec-
trophoretic properties. The tests varied depending on the type of pigment employed. Some tests showed that
toner components deposit both on negatively and posi-
tively charged electrostatic surfaces. A toner compo-
nent of this nature may still be useful, if it is combined
with the organosol, since in this case the toner charge
control is supplied by the high molecular weight resin.

An example of this follows:

EXAMPLE D

An organosol was conformed as before from the fol-
lowing:
37.5 gms. “PLIOLITE VTAC”
20.0 gms. “BETAPRENE BC-100”
100.0 gms. “SOLVESSO 100”
The matching toner component was made as follows:

50 gms. carbon black (particle size
25 millimicrons)
50 gms. BETAPRENE BC-100
25 gms. SOLVESSO 100

We stirred this mixture in a Cowles dissolver and
then milled the mixture in triple-roll mill. The mixture
was then diluted with “ISOPAR G” and the toner pro-
duced an immediate deposit on both positive and nega-
tively polarity electrosurface charges.

Twenty-five grams of the toner component was
added to the organosol solution and stirred with a
Cowles dissolver. The solution was then added to 1100
mls. of “ISOPAR G” in a high-speed emulsifying mill
and milled for three minutes.

The resultant adhesive toner concentrate was diluted
in the ratio of 50 mls. concentrate to 200 mls. of “ISO-
PAR G” to produce an adhesive developing liquid. This
adhesive developing liquid produced a deposit on nega-
tively charged zinc oxide photoconductor which was
then transferred completely to uncoated bond paper.
This formulation is characterized by a high-yield elec-
trophoretic deposition on a negative polarity charged
surface. The pigment to resin ratio of this toner is ap-
proximately 1:6.

It will be seen that a high molecular weight polymer
may form a solution which may be then suspended in
a diluent having low solvent power. “PLIOLITE
VTAC” acting by itself exhibits good adhesion to most
surfaces. We can modify the adhesive properties by
using other high molecular weight polymers which in
themselves have a lower adhesion for most surfaces.
Adhesion can be increased by adding tackifier resins
which impart additional adhesion to high molecular
weight polymers. Plasticizers may be added to modify
the adhesive properties, if such be desired.

The pigment component acts to reduce sedimenta-
tion of the toner concentrate. Our tacky toners gen-
erally comprise relatively large aggregates and conse-
sequently suffer greater sedimentation than liquid toners
of the prior art. This, however, does not present practi-
cal problems as long as the sediment is flocculent, since
such flocculent sediment is easily dispersed by me-
chanical agitation. It is for this reason that we have
shown an agitator in our developer tank.

It will be observed that, in general, we employ a high
molecular weight polymer which has a low adhesion for
the image-forming surface and a high adhesion for the
copy surface. We add another high molecular weight
polymer which acts as a dispersing agent to produce
optimum resin deposit and the required electrostatic
charge polarity. These resins in solution form an organ-
osol. If the high molecular weight polymer does not
have sufficiently high adhesion, we may add a tackifier
or a plasticizer which creates a high adhesion for the
copy paper. The resins and plasticizers which are
chosen must be insoluble in the diluent which suspends
the organosol and the toner formulation.

It will be seen that we have accomplished the objects
of our invention. We have provided a novel method of
contact transfer of developed electrostatic images from
the surface of a photoconductor to sheet material such
as paper. Our novel method enables such contact trans-
fer with a liquid developer to untreated paper. Our
transfer method of a developed electrostatically
formed image utilizes the tackiness of the toner and
does not depend on an electrostatic field. We have pro-
vided a method of contact transfer of a liquid toner de-
developed electrostatic image from a photoconductive
surface to a copy sheet while maintaining the conduc-
tive surface in a clean condition. We have provided a
liquid developer which has greater affinity for the copy
paper than the photoconductive surface on which the
image was formed. We have provided a photoconduc-
tive surface which has less affinity for the developed
electrostatic image than for the paper to which it is to
be transferred. We have provided a novel developing
liquid carrying in suspension a toner which is non-
sticky when first deposited, which becomes sticky or
tacky after deposit, so that it can be transferred in its
tacky condition, and which then loses its tackiness so
that it remains firmly bonded to the surface to which it
is transferred. We have provided a novel apparatus for
carrying out our novel method. We have provided a
novel sheet material having a special affinity for a tacky
toner developed image.

It will be understood that certain features and sub-
combinations are of utility and may be employed with-
out reference to other features and subcombinations.
This is contemplated by and is within the scope of our
claims. It is further obvious that various changes may
be made in details within the scope of our claims with-
out departing from the spirit of our invention. It is,
therefore, to be understood that our invention is not to
be limited to the specific details shown and described.

Having thus described our invention, what we claim
is:

1. In an electrophotographic apparatus a conductive
carrier, a photoconductive surface supported by said
carrier, means for charging said photoconductive sur-
face, means for exposing said charged surface to a pat-
tern of light and shade of an image to be reproduced to
form a latent electrostatic image, a tank for holding li-
quid toner, means for subjecting said latent electrostatic
image to the action of said liquid toner to form a tacky
image, transfer means for bringing sheet material into
contact with the tacky image while on said photocon-
ductive surface to transfer the developed image thereto,
and means for heating said sheet material before
said sheet material arrives at the contacting means.

2. Apparatus as in claim 1 in which said means for
heating said sheet material is positioned to direct heat
against the rear of said sheet material.
3,851,964

3. Apparatus as in claim 1 including means for removing excess toner from said photoconductive surface.

4. Apparatus as in claim 1 including means for cleaning said photoconductive surface after the operation of said transfer means.

5. Apparatus as in claim 1 including means for heating said tacky image to increase its tackiness.

6. Apparatus as in claim 1 including means for heating said transferred image on said sheet material to fix the same thereto.

7. Apparatus as in claim 1 in which said photoconductive surface has less affinity for the tacky image than said sheet material.

* * * * *