

1

2,863,767

XEROGRAPHIC METHOD

Robert G. Vyverberg, Pittsford, and James H. Neyhart, Rochester, N. Y., assignors to Haloid Xerox Inc., a corporation of New York

No Drawing. Application January 17, 1955
Serial No. 482,384

2 Claims. (Cl. 96—1)

This invention relates to xerography and relates particularly to an improved method of xerographic reproduction and a xerographic plate for use therein.

The art of xerography involves the utilization of a xerographic plate whose essential elements are a layer of photoconductive insulating material in continuous electrically coupled relation with respect to an electroconductive backing. The term photoconductive insulating material is applied to those substances which have the special property of being very high in insulating value when not exposed to light or other activating radiation but become conductive when exposed to activating radiation. The photoconductive insulating material being essentially non-conductive in the absence of activating radiation can have an electrostatic charge imposed thereon as by bringing it into operative relation with respect to a constant voltage corona spray, and the imposed voltage will be largely retained for a substantial period of time if the plate remains unexposed to activating radiation. Usually a positive potential is imposed on the exposed surface of the layer of photoconductive insulating material which may be in the neighborhood of 300 to 500 volts, or even higher. While a positive potential may thus be imposed, it is also possible to impose a negative potential.

If a xerographic plate which comprises the elements aforesaid has an electrostatic charge imposed thereon, then, upon exposing the surface of the layer of photoconductive insulating material to areas of activating radiation of different intensity, the electrostatic charge will be dissipated into the backing member to different degrees in the different areas, depending on the extent of the activating radiation exposure in these areas. The result of such exposure of the electrostatic plate to activating radiation is the production of an electrostatic latent image which can be used in various ways for reproducing in some visible form the latent image produced electrophotographically on the xerographic plate, such as a printed page, map, photograph or the like. In general, utilization of the latent image is effected by bringing into operative relation with the area on which the electrostatic latent image occurs particles which will be attracted to those areas where the electrostatic charge occurs, the accumulation of attracted particles being greater when the retained charge is greater. The so-attracted particles may thus be caused to correspond to the electrostatic latent image originally produced and may be used for direct printing or in providing other reproducing members whereby reproductions of the original subject to be reproduced may be made. After such use of a xerographic plate any residual finely divided material used to develop the electrostatic latent image is removed from the plate as by brushing or washing, whereupon the plate may be used again in a succeeding operational cycle comprising the charging of the layer of photoconductive insulating material and its exposure to activating radiation to produce an electrostatic latent image.

2

In the Carlson Patent No. 2,297,691 several photoconductive insulating materials for use in a xerographic plate are exemplified such as sulfur, anthracene, anthraquinone, mixtures of sulfur and selenium with sulfur predominating, and certain other sulfur-containing compositions. Subsequently it was found that vitreous selenium is much more responsive photoelectrically than the substances exemplified in the Carlson patent as photoconductive insulating materials. Ordinary metallic or crystalline selenium is a semi-conductor and, because of such conductive properties, is incapable of use in a xerographic plate. However, it was found that if selenium is deposited on the backing member of a xerographic plate under a high vacuum at a moderate temperature, for example, below about 170° F., the selenium is deposited in a vitreous condition that is amorphous or only very slightly crystalline, wherein it has a sufficiently high insulating value in the absence of activating radiation to permit of its use in a xerographic plate while at the same time providing a very high degree of responsiveness to activating radiation. Selenium when occurring in this form or condition is referred to herein as photoconductive vitreous selenium.

In commercial utilization of xerographic reproduction the activating radiation which is utilized in producing the latent electrostatic image on the xerographic plate commonly is daylight or artificial light such as that produced by an ordinary incandescent lamp or a lamp of the type commonly used in photography. However, other sources of activating radiation may be employed and among them are sources of X-ray radiation. Thus, X-rays that have been brought in to form an image or outline of an exposed subject as in conventional X-ray radiography likewise produce an electrostatic latent image on a xerographic plate.

While a xerographic plate comprising a layer of photoconductive vitreous selenium has very great utility in effecting high quality and rapid xerographic reproduction, it has been a serious source of inconvenience and practical disadvantage that xerographic plates suffer from fatigue, i. e., show impaired performance for an objectionably long period of time after having passed through an operational cycle comprising the charging of the plate and its exposure to activating radiation. Moreover, if any such xerographic plate is subjected to successive operational cycles the fatigue tends to continue to increase. The occurrence of fatigue is evidenced by substantial diminution of the capacity of the xerographic plate to accept an electrostatic charge and diminution of the capacity of the plate to retain an electrostatic charge when in the absence of activating radiation. Lack of capacity to retain an electrostatic charge in the absence of activating illumination is commonly referred to and is referred to herein as dark decay. Even in the case of a freshly prepared xerographic plate there is substantial dark decay such as 5% to 10% of the original charge over a period of about one minute. However, after a xerographic plate has become fatigued the fatigue is evidenced by an increase in the dark decay rate and the extent of the fatigue may be measured by comparing the dark decay over a stated period such as three or five minutes after one or more operational cycles with the dark decay in the case of a freshly prepared or fully recovered xerographic plate.

For obtaining preferred results the rate of dark decay should be about 5% or less for one minute. When the dark decay rate is not greater than about 10% for one minute the results obtainable are reasonably satisfactory. However, when the fatigue that has resulted from one or more operational cycles is such that the dark decay rate is 20% or more, the resulting impairment in effectiveness is a matter of serious concern.

Fatigue that has resulted from one or more operational cycles of a xerographic plate normally decreases upon passage of time and usually may be eliminated by permitting the plate to stand idle for a substantial period of time, such as overnight. However, in commercial application of xerographic reproduction it is not convenient to store plates for so long a time, and it is highly desirable to be able to keep using a plate again and again without anything more than a very short waiting period between operational cycles. While the recovery of a xerographic plate is most rapid immediately after the conclusion of a cycle, the rate of recovery decreases with the result that even after thirty minutes or so a substantial amount of fatigue persists. Such plate characteristics are a serious defect, especially when high contrasts are desired.

The fatigue problem that results from exposure to visible light differs in certain respects from that which results from X-ray exposure, the fatigue problem being especially troublesome in connection with xeroradiography. When the vitreous selenium layer of a xerographic plate is exposed to visible light a very substantial amount of fatigue results even from a single operational cycle, but upon successive cycles the total fatigue tends to level off. In the case of X-ray radiation, on the other hand, the fatigue from a single operational cycle may not be as great as that resulting from exposure to visible light, but there is a greater tendency for the fatigue to continue to accumulate when the operational cycles are repeated until the total fatigue becomes excessive. Moreover, there is a greater tendency to fatigue upon increase in the thickness of the selenium layer. Fatigue is especially troublesome when the thickness of the selenium layer exceeds 75 microns and for X-ray work the selenium layer generally runs over 75 microns and may even be as much as 300 microns. When a xerographic plate is activated by visible light the layer of photoconductive vitreous selenium usually ranges from about 10 to about 75 microns in thickness.

Another difference in the phenomena that occur as between light exposure and X-ray exposure is that in the case of light exposure fatigue produced thereby tends to be relatively uniform over the entire plate, with the result that poor acceptance and retention of an electrostatic charge is troublesome primarily because of the poorer contrasts that are obtainable. In the case of X-ray exposure the fatigue may be non-uniform in the pattern of the radiographed image and in such case one is troubled by residual image difficulties. X-ray fatigue is most noticeable when adjoining areas are exposed to X-ray radiation of much different intensity.

It is an object of this invention to provide a method whereby a xerographic plate of the character aforesaid may be continuously used in xerographic reproduction with only a very short resting period between operational cycles while at the same time eliminating the fatigue very substantially and even entirely and without injury to the plate. A further object of this invention resides in the provision of a xerographic plate which is especially made in such way as to be suitable for use in the practice of this invention.

It has been found according to this invention that recovery from fatigue can be greatly accelerated by subjecting the layer of photoconductive vitreous selenium to elevated temperature. At the elevated temperature employed, the recovery rate of the selenium layer becomes so greatly increased that the fatigue can be reduced substantially to zero even though the heating of the layer is so limited as to temperature rise and duration that there is no substantial impairment of the insulating characteristics, i. e., low dark conductivity of the vitreous selenium layer. Vitreous selenium when exposed to a relatively low order of temperature such as from about 150° F. to about 200° F. tends to become converted to the more crystalline semi-conductive form which is in-

operative for xerographic purposes, the rapidity of the conversion increasing as the temperature is increased. Even lower temperatures have an adverse effect on the high insulation characteristics that are a prerequisite of a xerographic plate. However, according to this invention it has been found, for example, that if a fatigued xerographic plate is subjected to a temperature ranging from about 110° F. to about 140° F. the fatigue recovery is so greatly accelerated that virtually complete recovery is made possible while at the same time there is no substantial increase in dark conductivity or other impairment of the xerographic plate. The time during which the plate is held within the temperature range indicated is brief, usually only about one to two minutes. It is thus seen that the heating step for accomplishing fatigue recovery according to this invention may be readily worked into a commercial operation wherein a xerographic plate is used in repeated operational cycles without affecting efficiency to any substantial extent.

In the practice of this invention it is preferable to bring the selenium layer of the xerographic plate from ambient atmospheric temperature up to the fatigue recovery temperature as rapidly as possible, e. g., in about 15 seconds, although a longer heating time of the order of 30 seconds to one minute is not excessive. The heating of the selenium layer may be accomplished in any suitable way. However, it has been found that fatigue recovery is especially effective when the xerographic plate is heated by exposing the back of the backing member of the plate to heat-imparting energy. Thus by providing the back of the backing member with a black coating or other coating having a high absorbing value for infra-red radiation and by exposing this coating to infra-red radiation the plate can be heated to fatigue recovery temperature under conditions that are especially favorable to fatigue recovery. On the other hand, when the selenium layer was directly exposed to infra-red radiation the fatigue recovery was counteracted by the direct action of the infra-red rays on the selenium coating. After the plate has been brought to the heat recovery temperature then the intensity of the heat to which the plate is subjected may be very greatly reduced and that amount only is used which is required in order to hold the plate within the fatigue recovery temperature range. For example, the xerographic plate may be subjected to heat as by infra-red radiation imposed on the back of the backing member for a sufficient time to bring the selenium layer up into the fatigue recovery temperature range. Thereafter the infra-red radiation can be greatly reduced or, alternatively, the plate may be moved from the infra-red radiation source to another location where the plate may be exposed either to radiation or a heated atmosphere which is appropriate to maintain the plate in the fatigue recovery temperature range. It is also possible to continue the initially applied heat sufficiently in the fatigue recovery temperature zone so that in the course of ordinary cooling and with no further supply of heat energy the plate will remain in the fatigue recovery temperature zone long enough to afford a satisfactorily complete elimination of fatigue.

The fatigue recovery may be effectively accomplished in only a short period of time, and normally it is preferable that the xerographic plate be maintained at elevated fatigue recovery temperature for about one to two minutes. In order to effect substantially full fatigue recovery a period of at least about forty-five seconds usually is required. However, even if the period is of substantially lesser duration, substantial fatigue recovery is accomplished. Usually it is preferable to discontinue the elevated fatigue recovery temperature after about 2½ to 3 minutes, for if the plate is held at elevated fatigue recovery temperature for a substantially longer period the dark conductivity of the selenium may become undesirably increased. The dark conductivity referred to

is that which is inherent from the physical state of the selenium as distinguished from the temporary effect of fatigue in increasing the rate of dark decay.

In order to minimize the possibility of increasing the dark decay rate for reasons other than fatigue, it likewise is preferable, after completing the fatigue recovery step carried out at the fatigue recovery elevated temperature, to accelerate the cooling of the xerographic plate. Cooling to ambient atmospheric temperature may be accelerated in any suitable way as by blowing or other movement of air in contact with the plate.

The practice of this invention may be further illustrated by reference to the following typical example. A xerographic plate was subjected to operational cycling including production of latent electrostatic images by exposure to X-ray activation after charging until the X-ray fatigue had become much higher than suitable for xeroradiography. The xerographic plate was a conventional plate suitable for xeroradiographic use, the layer of photoconductive vitreous selenium being applied to a clean mirror-smooth aluminum backing. The fatigued plate, whose recovery normally would require several hours, was subjected to infra-red radiation produced by six 250 watt infra-red lamps. The back of the xerographic plate had been coated with a black paint so as more effectively to receive the infra-red radiant energy and convert it into heat; and under the conditions mentioned the plate was heated from an ambient temperature of about 75° F. to a temperature of about 130° F. in slightly less than 15 seconds.

After such heating of the plate to bring it up to 130° F. the applied heat was diminished so as to hold the plate at about 130° F. for about one minute. Thereupon the plate was cooled by blowing air thereon so as to return it to a temperature of about 80° F. in about 30 seconds. It was found that all trace of fatigue had been eliminated.

It is to be understood that the foregoing example is merely illustrative of what is regarded as typical of preferred practice of this invention. The precise manner of heating, the degree of heating, the duration of the heating and the manner of cooling may be varied according to the principles that are described herein. Thus in the lower portion of the fatigue recovery temperature range the rate of fatigue recovery is somewhat lower than is the case in the upper range, but it also is the case that the lower temperatures have less tendency to cause crystal growth in the selenium with the result that in the lower portion of fatigue recovery temperature range longer periods of exposure to such temperatures are permitted so that the desired fatigue recovery may be accomplished. By way of further illustration, if the fatigue recovery temperature is about 115° F., then it is desirable to hold the plate at about this temperature for about 1½ to 2 minutes. Conversely, in the upper portion of the fatigue recovery temperature range a shorter heating period is possible and likewise is desirable for at the higher temperatures any tendency to promote undesired selenium crystallization is correspondingly greater.

While recovery from X-ray fatigue has been exemplified above, essentially the same treatment accomplishes in a like manner recovery from fatigue produced by visible light in the production of electrostatic latent images. More generally, it is apparent that according to this invention fatigue induced by exposure to activating radiation after charging may be largely or wholly eliminated by a simple and rapidly carried out heating step that has been found not only to be very effective for eliminating fatigue but also to be outside of those conditions that induce substantial impairment of the properties and characteristics of the plate.

While reference has been made hereinabove to the treatment of a xerographic plate, it is to be understood that in so far as the fatigue phenomenon is concerned

it is the layer of vitreous selenium that is involved and that the backing member, therefore, is largely immaterial. Thus the backing member may be composed of metals other than aluminum such as magnesium, brass, steel and the like. Moreover, a backing member may be used which is composed of a substance such as paper, glass or plastic that has been impregnated or coated with a suitable conducting substance such as a conductive metal or a conductive metal compound. In fact, it is not essential that the backing member be one which comprises built-in electroconductivity. For example, if the selenium layer is applied to a paper sheet and if an electrostatic charge is imposed thereon, the charge may be dissipated effectively if the paper sheet is temporarily placed in such relation to a conductive member that a continuous electrically coupled relationship is afforded. Similarly, any preformed plate may be employed wherein electroconductive material comprised in the backing member is in continuous electrically coupled relation with respect to the layer of vitreous selenium. However, for purposes of effecting rapid and effective heating the employment of a xerographic plate wherein the backing is preponderantly metallic is normally to be preferred. The layer of selenium is that which is of utility in xerography, i. e., selenium that is substantially free of halides or other impurities which tend to impart undue conductivity, the selenium being applied to provide a substantially uniform layer on a smooth surface of the backing member that is free of visible imperfections and preferably is of mirror-smoothness.

The nature of the phenomena that are involved in connection with fatigue in the use of a xerographic plate is not definitely known and it is to be understood that the nature and scope of this invention is not to be regarded as dependent upon any theoretical considerations expressed herein. However, there is some evidence indicating that the phenomenon of fatigue is caused by a number of carriers becoming trapped in the vitreous selenium during the operational cycle of charging and exposure to activating radiation. When the vitreous selenium layer is subjected to the fatigue recovery steps herein described and exemplified it is believed that trapped conductors are dissipated and perhaps are rendered free to combine with untrapped holes whereby the adverse fatigue effects are wholly or largely eliminated. It is also believed that the fatigue recovery phenomena are induced and accelerated by the heating step as described herein while still avoiding those somewhat more severe conditions that are known to convert vitreous selenium to the semi-conductive type that is inoperative for use in xerography.

We claim:

1. In a method of xerographic reproduction wherein a xerographic plate comprising a layer of photoconductive vitreous selenium in continuous electrically coupled relation with an electroconductive backing member is repeatedly subjected to an operational cycle which comprises imposing an electrostatic charge on its surface to sensitize the plate, exposing the sensitive plate to produce an electrostatic latent image thereon of electrostatic charges in image formation and taking off an image corresponding to said electrostatic latent image with the resultant occurrence of fatigue of said plate upon completion of an operational cycle, the improvement comprising accelerating recovery before repeating an operational cycle of the fatigued xerographic plate comprising between said operational cycles heating said plate to bring it to a temperature in the range from about 110° F. to about 140° F. in not greater than about one minute and maintaining said layer at a temperature within said range from about ¾ to 3 minutes until substantial recovery of said layer has been effected, and then in not greater than about one minute cooling said plate to at least about 80° F., the heat to which said layer is subjected to bring it up to said temperature within said range being substantial-

ly greater than any heat to which said layer is subjected to maintain its temperature within said range.

2. In a method of xerographic reproduction wherein a xerographic plate comprising a layer of photoconductive vitreous selenium in continuous electrically coupled relation with an electroconductive backing member is repeatedly subjected to an operational cycle which comprises imposing an electrostatic charge on its surface to sensitize the plate, exposing the sensitive plate to produce an electrostatic latent image thereon of electrostatic charges in image formation and taking off an image corresponding to said electrostatic latent image with the resultant occurrence of fatigue of said plate upon completion of an operational cycle, the improvement comprising accelerating recovery before repeating an operational cycle of the fatigued xerographic plate comprising between said operational cycles heating said plate from atmospheric temperature to a temperature in the range from about 115° F. to about 130° F. in not more than about 30 seconds, maintaining its temperature within said range for about

¾ to about 2 minutes and then subjecting the plate to accelerated cooling reducing its temperature to about 80° F. within about 30 seconds.

References Cited in the file of this patent

UNITED STATES PATENTS

2,476,042	Hewlett	July 12, 1949
2,543,046	Murray	Feb. 27, 1951
2,662,832	Middleton et al.	Dec. 15, 1953
2,663,636	Middleton	Dec. 22, 1953
2,711,481	Phillips	June 21, 1955
2,798,960	Yeates	July 9, 1957

OTHER REFERENCES

"Photo-Conductivity"—Nix; Reviews of Modern Physics; October 1932; vol. 4, pp. 723-766; page 730 particularly relied upon.

Physical Review, vol. 76, 1949, p. 179. Copy in (SL).