May 3, 1966 K. A. METCALFE ETAL 3,249,430
PROCESS FOR PRODUCING IMAGES IN ELECTROPHOTOGRAPHY AND RADIOGRAPHY
Filed Aug. 2, 1961 3 Sheets-Sheet 1

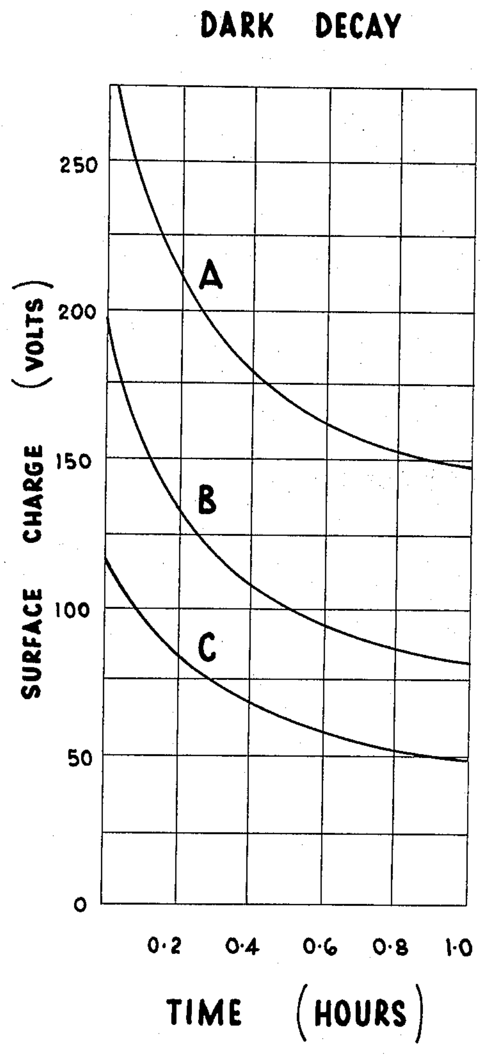

FIG 1

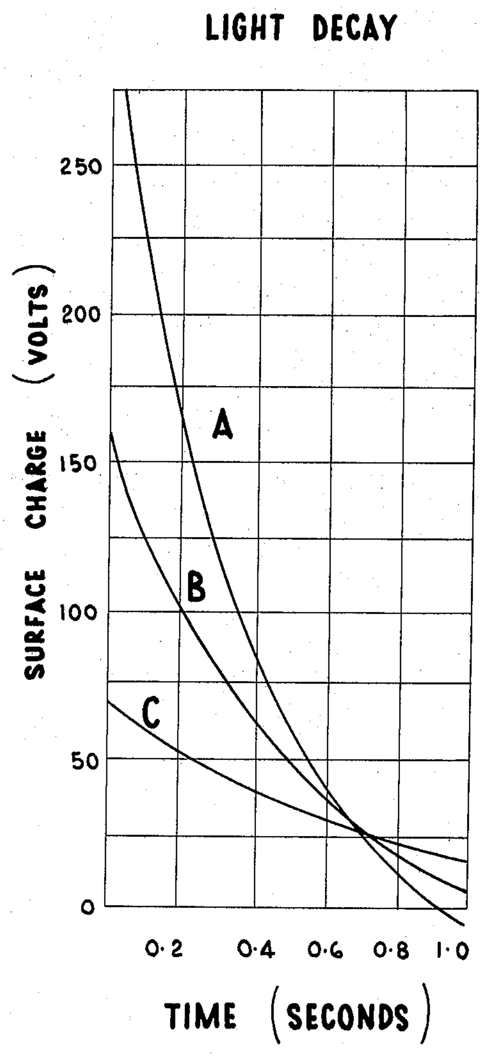

FIG 2

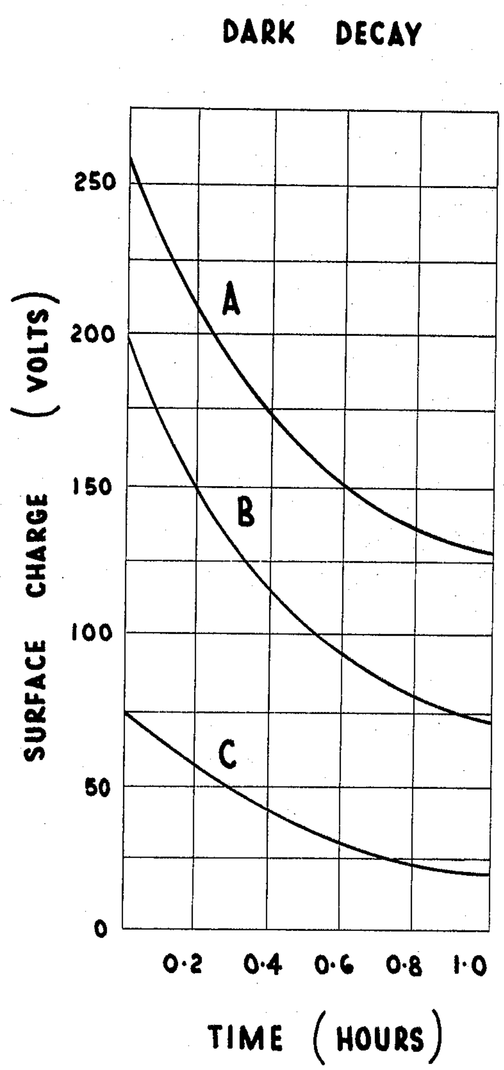
DARK DECAY
SURFACE CHARGE (VOLTS)
250
200
150
100
50
0
A
B
C
0·2
0·4
0·6
0·8
1·0
TIME (HOURS)

FIG 3

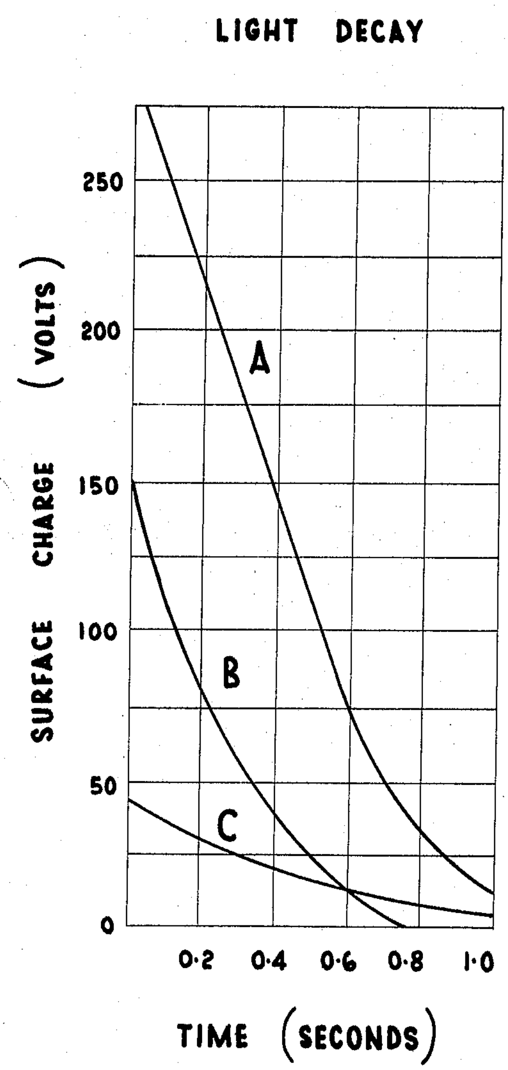
LIGHT DECAY
SURFACE CHARGE (VOLTS)
250
200
150
100
50
0
A
B
C
0·2
0·4
0·6
0·8
1·0
TIME (SECONDS)

FIG 4

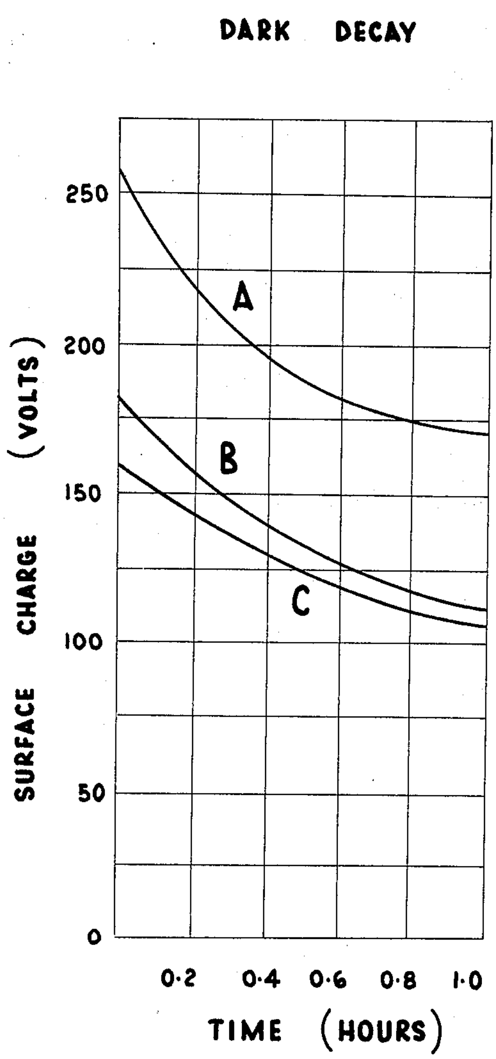
DARK DECAY
250
200
150
100
50
0
A
B
C
SURFACE CHARGE (VOLTS)
0·2
0·4
0·6
0·8
1·0
TIME (HOURS)

FIG 5

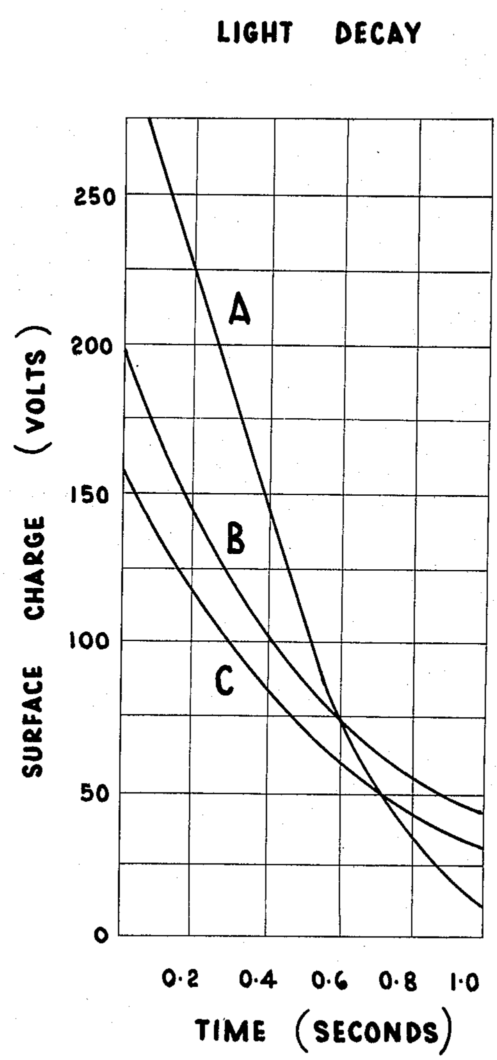
LIGHT DECAY
250
200
150
100
50
0
A
B
C
SURFACE CHARGE (VOLTS)
0·2
0·4
0·6
0·8
1·0
TIME (SECONDS)

FIG 6

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PROCESS FOR PRODUCING IMAGES IN ELECTROPHOTOGRAPHY AND RADIOGRAPHY

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4 Claims. (Cl. 96—1)

This invention relates to an improved process for controlling contrast when producing images in electrophotography and radiography.

The customary method of producing an image in electrophotography and radiography is to charge a xerographic paper or film by subjecting it to a corona discharge and to then light-modify the charged medium, after which development is carried out by any of the known xerographic processes.

Various ways of controlling the contrast have been proposed heretofore, such as controlling the rate of decay of the image during development, or controlling the voltage applied to the electrostatic image.

We have now found that an improved image and an improved form of control for producing such an image is possible by pre-conditioning the photo-conductor surface by electromagnetic waves, such as light waves.

We have found for instance that by pre-exposing xerographic surfaces to a relatively strong light or other electromagnetic wave, the xerographic surface is conditioned so that both the charge holding ability, i.e., the amount of charge for a given voltage which can be held by the xerographic surface and its charge leakage rate is decreased.

Thus a longer and more intense charging period is required to reach the surface charge limit, and this intense charging will not create surface conduction defects such as Lichtenberg figures, thereby assuring a better and cleaner image as well as one in which contrast can be controlled by the degree of conditioning.

The invention therefore consists in the method of controlling contrast of a xerographic image which embodies the steps of first exposing a photo-conductor surface to electromagnetic waves which can be absorbed by the photo-conductor whereby both its charge holding ability and its leakage rate is decreased, then charging the so modified photo-conductor in the absence of light by subjecting to a corona discharge to produce a uniform electric charge on the photo-conductor, then exposing the surface to electromagnetic waves of the required pattern to differentially bleed away the charge and produce an electrostatic image, and then developing the electrostatic image by applying a developer which deposits according to the electrostatic pattern.

It would appear that for practical purposes, visible light gives a very desirable improvement to a xerographic image when the photo-conductor medium is first pretreated prior to the production thereon of the xerographic image, but it is also clear that electromagnetic waves of greatly varying wave lengths, such as X-rays, also have a similar effect. It is advantageous to use electromagnetic waves having a wave length in the vicinity of the absorption bands of the material.

The invention thus shows that when a photo-conductor medium is subjected to pre-exposure to a relatively strong light, or other electromagnetic wave, the photo-conductor medium is rendered more conductive than it is when it is dark-rested. This has the effect that when it is subjected

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to electrons, the electrons result in a lower flux density immediately above the zinc oxide layer which is equivalent to a much lower voltage on the surface while the modified condition maintains.

The amount of light or other electromagnetic wave used for conditioning is much greater than for exposure. During exposure light must be affecting areas which have already yielded charge carriers. The secondary yield of carriers, namely the second exposure, is taking place from material deficient in easily produced carriers so the yield per photon is less. This means that there is a lower decay rate for conditioned areas.

The conductive backing or substrate which is otherwise necessary between the paper or other backing and the photo-conductor medium is not necessary when this invention is practised, the photo-conductor medium itself acting as the conductive backing so that a relatively low charge only can be maintained on the immediate outer surface of the photo-conductor material. When the image is subsequently light-modified to produce the picture, a much better electrostatic image results for subsequent development as only the upper surface appears to hold a charge. To prove this, the photo-conductor medium was applied to an insulating film without a conductive backing and, only when pre-modified by light, could a satisfactory picture be obtained.

As previously stated herein, while a photo-conductor medium such as zinc oxide, which is highly sensitive to light conditioning by visible rays of light, provides an effective medium for carrying the invention into effect, the same effect exists with materials which can be preconditioned by exposure to electromagnetic waves to cause the materials to be what we term "fatigued" or electromagnetic wave conditioned to charging by electron means in their pre-conditioned state with better controlled development of such an image by xerographic means.

To allow the invention to be fully appreciated, curves showing dark and light decay characteristics of zinc oxide paper under different pre-exposure conditions will now be referred to, the curves being designated FIGURES 1 to 6 and showing respectively the effects of pre-treatment of dark-rested xerographic paper, and the image exposure curves where the paper is exposed to various degrees and sources of electromagnetic energy.

In FIGURE 1 the surface charge remaining on a zinc oxide papers is shown by the curves A and B and C respectively where in curve A the paper has been dark-rested to remove fatigue of the zinc oxide, in curve B a pre-exposure for 10 seconds to visible light has been made, and in curve C a pre-exposure of 30 seconds to visible light has been made, the source of illumination in each case being a 160 watt actinic lamp spaced at six inches from the zinc oxide paper, giving a luminance of 1,130 candles per square foot.

It will be obvious in this that at the instant of charging the voltage in curve A is approximately 300 volts, whereas cuve B is down to 200 volts while curve C has dropped to approximately 120 volts.

As the paper is dark rested for half an hour, the charge drops down respectively to 170 volts, 100 volts, and 65 volts, while after one hour of dark resting, the respective voltages are 150, 80 and 50 volts.

In FIGURE 2 the voltages are shown where the photo-conductor is charged in a similar manner but the paper is then exposed to light of 200 candles per foot to give a light decay curve, in which case it will be noted that curves A and B after one second have dropped down materially below curve C which itself remains almost unaltered in its slope under the conditions of both FIGURE 1 and FIGURE 2.

It will be noted that in FIGURES 1 and 2 there is a difference in starting voltages of the various curves, due to the difficulty of obtaining uniform zinc oxide coatings and also due to measuring problems over the short time available in the light decay cycle.

In FIGURE 3 the surface charge remaining on the zinc oxide paper is again shown by curves A, B and C respectively wherein curve A the paper has been dark-rested while in B a pre-exposure of 2.5 seconds has been made, the ultra violet source being a 125 watt "Hanovia" black lamp with filter placed 10 inches from the paper while C shows the curve where a 30 second exposure to the same ultra violet source was made.

These show that the voltage curve for A, B and C commence respectively at 250, 200 and 75 volts approximately.

After one hour of dark resting the voltages have dropped respectively to approximately 130 volts, 74 volts, 20 volts.

In FIGURE 4 the voltages are shown where the photoconductor is electrically charged in a similar manner but the paper is dark rested in curve A, has an exposure of 2.5 seconds to an ultra violet light source before charging in curve B. In curve C a 30 second exposure was used under similar conditions, showing that the effective light then is very materially altered. Curve A shows that a high charge can be taken initially where no pre-treatment with ultra violet light has existed, but the charge has bled away almost completely in one second. Where a short pre-charge under ultra violet light has taken place as in case B the electrical resistance of the zinc oxide film has been altered so that now only approximately 150 volts can be held for the same charge effect, and this again bleeds away in something under a second.

Where the ultra violet pre-conditioning has been carried out for 30 seconds, it will be noted that the electrical resistivity is now altered so that the same electrical charging means can only raise a voltage of below 50 volts on the zinc oxide but after one second of exposure to light the paper still holds a charge and continues to do so for a considerable time thereafter.

FIGURES 5 and 6 are similar to FIGURES 3 and 4 except that the pre-treatment of the paper has now been carried out with X-rays, the charging having been effected under curve B by exposure for ten milliampere minutes to 120 kv. at a distance of 12 inches.

In curve C the exposure was four minutes to the same X-ray source.

It is to be noted that in all of the figures the curve marked A, which is the normal zinc oxide curve for the particular conditions, remains somewhat the same, there being a variation of course in test papers and conditions giving some fluctuation in the curve.

Some amount of pre-energization with electromagnetic waves as shown by curve B has lowered the amount of electrical charge the zinc oxide can support and the decay curves follow a somewhat different pattern before charging, the amount of charge which can be held has obviously been reduced but the dark decay figures show that the charge is similarly held better in the heavily pre-treated paper and therefore a considerable difference in picture holding capacity exists. A lesser degree of contrast is possible because of the flatter curves.

With regard to the range within which the preconditioning operates it can be stated that this would be effective for any electromagnetic wave, but for best results it is desirable to use a wave length which corresponds approximately to an effective absorption edge of the material being fatigued or pre-treated.

In this way zinc oxide can suitably be treated by electromagnetic waves of a wave length somewhere between 3,000 to 4,000 angstrom units, the greatest effect of course being where there is the greatest absorption of the radiation.

With selenium the best effects obtainable are between 3,000 and 6,000 angstrom units, from which it is to be noted that zinc oxide can be effectively treated by visible light which ranges from approximately 4,000 to 7,000 angstrom units and similarly selenium can also be treated by such light.

Both zinc oxide and selenium react effectively to ultra violet radiation, that is in the range between 3,000 and 4,000 angstrom units. This effect, with zinc oxide, is shown by the graphs of FIGURES 3 and 4.

While X-rays are effective, a wave length should preferably be chosen where the rays are most easily absorbed by the medium being conditioned, and it is to be noted for instance that for zinc oxide there is an absorption edge of somewhere about 1.28 angstrom units while for lead the effective edge would be at approximately .949 angstrom unit, in which case again X-rays which normally have a range from 0.1 to 100 angstrom units would be useful.

Gamma rays with an angstrom range of 0.005–1.40 are similarly suitable with materials where there is an absorption edge within this range, but generally the shorter wave length requires a longer time element to effect the conditioning of the materials.

In the upper range, that is in the infrared or heat range of above 7,000 angstrom units the effect still exists, and it seems clear therefore that any electromagnetic wave can be used to condition materials prior to using them in xerographic processes, the particular wave length preferably being chosen according to where the greatest absorption of the radiation will result.

The following examples show how the invention can be applied.

Example 1

(1) Zinc oxide on bond paper backing, with coating comprising 75% zinc oxide and 25% resin by weight, such as a linseed oil modified resin for example a short oil alkyd resin. The coating is applied by known methods such as electrostatic coating.

(2) This surface is *exposed* to light over its entire area, the light being that from 160 watt "blue actinic" lamp held 6 inches from the surface for 30 seconds.

(3) The surface is then *charged* in a charging device in which the electric field strength between the discharge points and the base electrode is 10,000 volts per inch, the charging time being 10 seconds.

(4) The surface is then exposed to an optical image in a normal manner as in ordinary photography an example being a contact print of continuous tone material for 3 seconds at two feet from a 160 watt "blue actinic" lamp.

(5) The surface is then *developed* with a standard developer as is well known in the following composition:

	Grams
Pentarol 20	15
Rhodene L6/100	15
Kerosene	25
Carbon black	60
Waxoline nigrosine	15

This is prepared in the normal manner and dispersed in the hydrocarbon solvent known under the trademark "Shellite."

Pentarol 20 is a phenol modified pentaerythritol ester of resin, acid value 7–15, specific gravity 1.09 at 20° C., melting range 110–120° by Polymer Corporation Interstate Pty. Ltd.

Rhodene L6/100 is a linseed oil modified alkyd resin oil length 52%, acid value 6–10, specific gravity 0.965 at 20° C. by Polymer Corporation Interstate Pty. Ltd.

Shellite in an aliphatic hydrocarbon solvent by the Shell Company.

(6) The *resultant* image is characterized by a low contrast wide latitude, soft image, covering a density range of not less than 3.0, with minimum grain due to paper backing.

Example 2

Step:

1. Use zinc oxide on art paper,
2. 10 seconds instead of 30 seconds,
3. Result is characterized by higher contrast of the order of density range 1.3.

Example 3

Step 1. Use zinc oxide with 10% bismuth trioxide and then as in 1.

Example 4

As in Example 1, but expose to X-rays instead of light in step 4, for example to 140 kv. X-rays for two minutes through aluminum casting, the result is characterized by a radiograph of wide latitude and little paper grain.

Example 5

Use selenium, amorphous variety, vacuum evaporated on glass to 50 microns thickness.

In step 2 expose for two seconds,

In step 4, expose for one second.

The result is characterized by soft tones, wide latitude and absence of flaws due to electrical exaggeration of defects at the interface.

Example 6

Use zinc oxide or selenium on a polyester film base without conductive substrate.

The process is carried out as in Example 1 or 5. Result is production of a relatively conductive interface or substrate and a wide latitude picture without the normally encountered non-image patterns such as Lichtenberg figures and confusion zones.

What we claim is:

1. The method of controlling contrast of a xerographic image which consists of the steps of first uniformly pre-exposing a photo-conductor surface to high intensity electromagnetic waves of a wave length which can be absorbed by the photo-conductor and to which the surface is sensitive whereby the photo-conductor is fatigued so that both its charge holding ability and its leakage rate is decreased, subsequently charging the thus fatigued photo-conductor in the absence of light by subjecting the photo-conductor to a corona discharge to produce a uniform electric charge on the photo-conductor, then exposing the photo-conductor to electromagnetic waves of the

required pattern to differentially bleed away the charge and produce an electrostatic image, and then developing the electrostatic image by applying a developer which deposits according to the electrostatic pattern.

2. The method according to claim **1** wherein the electromagnetic waves are in the visible light range between about 4,000 to 7,000 angstrom units and the material being conditioned is a zinc oxide photo-conductor, the pre-exposure being to an electromagnetic wave in the light range between 4,000 to 7,000 angstrom units of effect equal to at least an intensity and duration of 1,130 candles per square foot acting for 30 seconds.

3. The method according to claim **1** wherein the electromagnetic waves are in the ultra violet range between about 3,000 to 4,000 angstrom units and the material being conditioned is a zinc oxide photo-conductor, the pre-exposure effect being equal to at least an intensity and duration of an ultra violet lamp of 125 watts at 10 inch spacing for 30 seconds.

4. The method according to claim **1** wherein the electromagnetic waves are in the X-ray range between 0.1 and 100 angstrom units and the material being conditioned is a zinc oxide photo-conductor, the pre-exposure effect being equal to at least an intensity and duration from an X-ray tube at 120 kv. at 12 inch spacing for ten milliampere-minutes.

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