

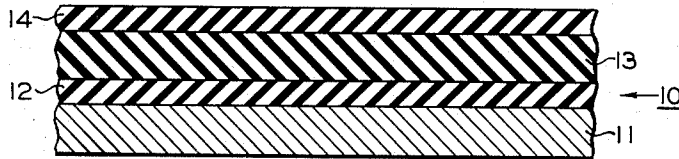
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XEROGRAPHIC PLATE

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1

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XEROGRAPHIC PLATE

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This invention relates in general to the art of xerography, and, in particular, to a sensitive plate therefor. More specifically, the invention relates to a new xerographic member comprising a conductive backing having on at least one surface thereof a coating of arsenic trisulfide, which in turn is covered by a coating of a photoconductive insulating material, which member is known as a xerographic plate.

In the art of xerography it is usual to form an electrostatic latent image on a member or plate which comprises a conductive backing such as, for example, a metallic surface, and having a photoconductive insulating surface thereon. It has previously been found that a suitable plate for this purpose is a metallic member having a layer of vitreous selenium. Such a plate is characterized by being capable of receiving a satisfactory electrostatic charge and selectively dissipating such a charge when exposed to a light pattern.

While such a plate has become the commercial standard in the xerographic art, it is subject to certain limitations. Thus, due to an extremely rapid loss of potential when stored in the dark (termed "dark decay") for a negative charge the use of selenium plates is largely restricted to positive charging. Furthermore, when selenium plates are used with extremely penetrating radiation, such as X-rays, the dark decay increases enormously after exposure to the penetrating radiation. Thus, before the plate can be resensitized and used in another cycle of operation special measures must be taken to restore the plate to its insulating condition wherein an electrostatic charge will be satisfactorily retained in the dark. In practice, this requires resting the plate for appreciable periods of time.

Now, in accordance with the present invention, it has been found that an improved xerographic plate can be prepared by depositing a layer of arsenic trisulfide between the conductive backing and the photoconductive insulating layer. The plate, as thus modified, may be used equally with both positive and negative charging without loss in spectral sensitivity and exhibits an astonishing degree of freedom from fatigue when used with penetrating radiation.

The new and improved plates of the present invention can be prepared by a variety of methods. For example, the separate layer of arsenic trisulfide and photoconductive insulating material may be applied by evaporation onto the plate under high vacuum, by spraying on the desired surface in molten form, by flame deposition (de-

2

composing a volatile organic compounds when in contact with the surface on which the coating is made), etc. If desired a transparent insulating coating as of a vinyl resin, a cellulose ester or ether, a silicone resin, silicon monoxide, etc. may be coated on top of the xerographic plate to protect the surface thereof from abrasion and mechanical damage.

While selenium is the preferred photoconductive insulating material, other known photoconductive insulating materials as anthracene, sulfur and various alloys of selenium such as mixtures of selenium and tellurium, selenium and arsenic, selenium and gallium, etc. may be used as the photoconductive insulating layer. In addition, the photoconductive insulating layer may, if desired, be itself formed in discrete layers each layer containing a different type of photoconductive insulating material. One such combination would be a layer of vitreous selenium immediately in contact with the arsenic trifluoride while on top of the vitreous selenium would be placed a layer of a mixture of about 20% tellurium and 80% selenium by weight. Other photoconductive insulating materials and combinations thereof known to those skilled in the art may be used in preparing the novel plates of the instant invention.

The drawing is a section of a xerographic plate prepared according to the invention. As shown, a xerographic plate 10 according to the instant invention, comprises a conductive backing 11 having coated thereon a thin relatively uniform layer 12 of arsenic trisulfide which in turn is covered by a layer 13 of a photoconductive insulating material. If desired, the photoconductor 13 may be covered by a protective coating 14.

The general scope and nature of the invention having been set forth the following examples are given as typical illustrations of methods by which the desired plates may be prepared.

EXAMPLE 1

A brass plate was polished with Glass Wax (a trade name of the Gold Seal Company, Bismarck, North Dakota, for a composition comprising about 75% water, 15% naphtha, 7.5% abrasive, and the balance ammonia, emulsifier, and coloring agent), rinsed in isopropyl alcohol and then degreased in hot isopropyl alcohol vapor. A mask was placed over half of the plate. The plate was then attached to a platen about four inches above a molybdenum boat. Yellow orpiment-arsenic trisulfide obtained from the Coleman and Bell Company, Norwood, Ohio, was placed in the boat and a bell jar placed over the apparatus. The system was then evacuated to a pressure of approximately 0.5 micron of mercury and the arsenic trisulfide evaporated onto the plate. The vacuum was then broken, the mask removed from the plate and another molybdenum boat containing selenium was placed in the apparatus, the bell jar replaced and the system evacuated to a pressure of approximately 0.5 micron of mercury and the selenium deposited on the plate.

The thickness of the films on the plate was then measured. The arsenic trisulfide was about 1.5 microns thick while the selenium was about 35 microns thick. The plate was placed in the dark and charged negatively by

corona emission. The amount of charge on the plate was then measured with an electrometer. The plate was kept in the dark for some time during which several measurements were made of the charge on the plate to determine the dark decay taking place.

In the case of the selenium only portion of the plate, the dark decay was so rapid that plate potential had fallen off to 60 volts before it could be measured, while in the case of the portion of the plate having an interlayer of arsenic trisulfide the initial reading was 500 volts. The dark decay half-time from these initial potentials measured in seconds were 20 for the selenium only portion of the plate and 817 for the portion having the arsenic trisulfide interlayer.

The experiment was then repeated using positive corona emission to charge the plate. With positive charging both the selenium only and the arsenic trisulfide interlayer portions of the plate accepted an initial potential of 500 volts. However, the dark decay half-time was 650 seconds for the selenium only portion and 2,220 seconds for the portion with the arsenic trisulfide interlayer.

The sensitivity of the two portions of the plate to light of various wave lengths was then determined for both positive and negative sensitization. The light intensity for all wave lengths was 0.03 microwatt per centimeter. The sensitivity was computed by the standard method of using the reciprocal of the time for the potential to drop to one-half its initial value (from V_0 to $V_0/2$) under exposure to this light intensity. The formula is

$$S = \frac{V_0^{1/3}}{2T_d I^{0.9}}$$

where S equals sensitivity, T_d is the time in seconds for the potential drop to one-half its initial value (from V_0 to $V_0/2$), V_0 is the initial potential and I is the light intensity. Using these figures with a monochromatic light source neither portion of the plate displayed a measurable sensitivity for either positive or negative charging for wave lengths of either 600 or 700 millimicrons.

For negative charging the dark decay was too rapid to permit measurement of sensitivity at any wave length for the portions of the plate having only selenium. In the portion of the plate having an arsenic trisulfide interlayer it was found that the plate had a sensitivity of 2.1 at a wave length of 500 millimicrons and of 7.8 at 400 millimicrons.

For positive charging the portion of the plate having only selenium had a sensitivity of 3.9 at 500 millimicrons and 13.4 at 400 millimicrons. In contrast, the portion having an arsenic trisulfide interlayer had sensitivities of 4.2 at 500 millimicrons and 18.7 at 400 millimicrons.

EXAMPLE 2

A plate was prepared as in Example 1 except that the arsenic trisulfide interlayer was less than one micron thick while the selenium remained at 35 microns.

In this plate for positive charging charge acceptance for both portions of the plate was 500 volts. However, the dark decay half-time was only 460 seconds for the selenium only portion but 29,000 seconds for the arsenic trisulfide interlayer portion. The selenium only portion of the plate had a sensitivity of 4.7 at 500 millimicrons and 13.4 at 400 millimicrons while the portion having the arsenic trisulfide interlayer had sensitivities of 2.7 at 500 millimicrons and 12.6 at 400 millimicrons.

For negative charging it was again almost impossible to measure the selenium only portion of the plate. The initial potential was only 60 volts and the dark decay half-time was only 32 seconds. In contrast, the portion of the plate having the arsenic trisulfide interlayer had a charge acceptance for negative charging of 450 volts, a dark decay half-time of 500 seconds, a sensitivity of 3.8 at 500 millimicrons and 10 at 400 millimicrons.

EXAMPLE 3

A plate was prepared as described in Example 1 except that in place of the Glass Wax treatment the plate was rinsed successively in benzene, isopropyl alcohol, and acetone prior to the degreasing in hot isopropyl alcohol vapor. The selenium coating was about 110 microns thick and the arsenic trisulfide interlayer was about 0.2 micron thick. This plate was used to test X-ray fatigue and sensitivity.

An objective measure of fatigue is obtained by dividing the difference in voltage on the plate before and after exposure to radiation (taken in each case three minutes after charging) by the voltage on the plate before exposure (three minutes after charging), expressing the ratio as a percentage. At no time during the fatigue measurements were the plates exposed to light and the plates were allowed to rest in the dark a minimum of seven hours between successive exposures to X-rays. After being allowed to rest in the dark for the prescribed period the plates were charged and the dark decay was observed for three minutes. The plates were then exposed to X-rays and after waiting for from a half minute to thirty minutes were again charged and the dark decay again observed for three minutes. In each case the 60 ma.-second exposure to X-rays was sufficient to decay the plates to zero potential. The X-ray tube was placed 36 inches above the plate and exposure was through a $\frac{1}{4}$ inch Bakelite window at 100 kilovolts.

In the case of the selenium only portion of the plate, the fatigue was 75% when measured one-half minute after exposure and was still 23.2% when measured 30 minutes after exposure. In comparison, the portion of the plate having an interlayer of arsenic trisulfide had a fatigue of only 15.4% when measured one-half minute after exposure and this had fallen to 0% fatigue at 10 minutes after exposure.

In this series of tests the plates were charged by corona emission to an initial potential of 1,000 volts as is usual in xeroradiography.

The fatigue tests were then repeated using negative charges to sensitize the xerographic plate. When the recharging occurred one-half minute after exposure, the fatigue on the selenium only plate was 76% falling to 27% when the charging occurred 30 minutes after exposure. On the portion of the plate having the arsenic trisulfide interlayer, when the charging occurred one-half minute after exposure, fatigue once again was 15.5% falling to 2.5% when charging occurred five minutes after exposure.

The X-ray sensitivities of the two portions of the plate were also determined in terms of the percentage rate of decay of original charge, i.e., percentage divided by seconds with the following results: A selenium plate positively charged had an X-ray sensitivity of 7.6 while the plate with the arsenic trisulfide interlayer had a sensitivity of 10.2 when positively charged and 17.0 when negatively charged.

EXAMPLES 4 THROUGH 6

Three plates were prepared, one having an aluminum backing, one aluminum covered with a coating of aluminum oxide approximately 40 angstroms thick and one having a chromium backing. The aluminum backing was cleaned by successive rinses in benzene, isopropyl alcohol, acetone and hot isopropyl alcohol vapor. In each case one-half of the plate was coated with arsenic trisulfide by vacuum evaporation as described in Example 1, the layer being about 0.5 micron thick, and then the entire plate was covered with selenium—again by vacuum evaporation. The selenium thicknesses were, respectively, 145 microns, 135 microns and 190 microns. Plates were then tested for initial charge acceptance, dark decay rate measured in volts per minute and sensitivity to both 400 millimicron and 500 millimicron wavelength radiation and fatigue. The fatigue test was the same as in Example 3

except that the radiation used was 400 millimicrons wavelength rather than X-ray radiation. The plate of Example 6 was also tested using negative charging. Results of these tests are set forth in the following table:

Table 1

Example	Film Composition	Charging Polarity	Initial Potential, volts	Dark-Decay rate, volts/min.	Sensitivity		Fatigue	
					400 m μ	500 m μ	0.5 min.	5.0 min.
4	Selenium Se-As ₂ S ₃ Interface	+	350	9	80	8.0	67.4	39
		+	400	6	43	9.7	5.6	0
5	do	+	300	7	19.5	9.8	18.5	1.7
		+	400	4	29	8.7	2.9	0
6	do	+	420	14	35	6.5	6.7	0
		+	420	2	30	11	0	
6	do	-	200	12.8	11	4.5		
		-	310	2	20	5.2		

EXAMPLES 7 THROUGH 9

Three plates were prepared, two having brass backings and one aluminum covered with a coating of aluminum oxide approximately 40 angstroms thick. In each case one-half of the plate was coated with arsenic trisulfide by vacuum evaporation as described in Example 1, the layer being about 0.5 micron thick, and the entire plate was then covered with vitreous selenium again by vacuum evaporation as described in Example 1. The selenium thicknesses were, respectively, 115 microns, 143 microns and 178 microns. The plates were then tested for initial charge acceptance, dark decay rate measured in volts per minute and sensitivity to both 400 millimicron and 500 millimicron wavelength radiation. Results of these tests, for both positive and negative charging, are set forth in the following table:

Table 2

Example	Film Composition	Charging Polarity	Initial Potential, volts	Dark-Decay Rate, volts/min.	Sensitivity	
					400 m μ	500 m μ
7	Selenium Se-As ₂ S ₃ Interface	+	425	13	29.5	6.8
		+	420	3	35	4.9
8	do	+	400	1.6	46	7.1
		+	420	1.0	36	10
9	do	+	370	1.6	45	7.5
		+	420	0.84	45	11
8	do	-	320	3	10	3
		-	225	15	35	4
9	do	-	340	11	10	4.4
		-	280	18.4	25	8.2

A conductive base plate is usually required for xerographic plates and metal forms the most suitable material. However, a high conductivity is not required and almost any structurally satisfactory material which is more conductive than the photoconductive layer can be used. Materials having electrical resistivities less than about 10¹⁰ ohms-cm. are generally satisfactory for the base plates of this invention although it is more desirable to use materials of less than about 10⁵ ohms-cm. Any gross surface irregularities, i.e. burns, tool marks, are removed from the base plate by grinding or polishing, although it is unnecessary to polish the plate until it has a mirror-like surface. The plate surface is cleaned before coating in order to remove grease, dirt, and other impurities which might prevent firm adherence of the coating to the base plate. This is readily accomplished by washing the plate with any suitable alkali cleaner or with a hydrocarbon solvent such as benzene, followed by rinsing and drying. Suitable base plate materials are aluminum, glass having a conductive coating thereon as of tin oxide or aluminum, stainless steel, nickel, chromium, zinc, etc.

Conductive plastic, conductively coated paper, or other web or film-like member may be used as the conductive supporting surface as desired. It is to be understood that the backing member selected for this plate may be in the form of a flat plate or may equally be in the form

of a cylinder, flexible sheet or other member having a surface suitable for the xerographic process.

The selenium used in the preparation of xerographic plates should be free of impurities such as copper, iron,

lead, and bismuth, which appear to adversely affect its ability to hold electrostatic charges, that is by forming conducting paths in the film or promoting the formation of conducting hexagonal selenium so that electrostatic charges leak off rapidly even in the dark and electrostatic deposition of powder or other finely-divided material cannot be obtained. Preferably, there should be used amorphous selenium available in pellet form $\frac{1}{17}$ inch to $\frac{1}{8}$ inch size under the name "A.R.Q." (ammonia reduced in quartz from selenium oxide) as manufactured, for this grade of selenium is essentially pure, containing less than about twenty parts per million of impurities. If purified, other grades of selenium, i.e. "D.D.Q." (double distilled in quartz) and "C.C.R." (commercial grade) as manufactured can likewise be employed in the process disclosed herein. To purify these grades of selenium,

they are first freed of copper, iron, lead, and bismuth by distillation. The selenium is next heated to about 250° C., slightly above its melting point, and, while molten, is then dropped through a shot tower (or in the laboratory by means of an eye dropper) into water to form pellets. The pellets are subsequently treated with petroleum ether to remove water and allowed to air dry. If desired, the purified selenium can be remelted and cast in boats to form sticks. It can also be reduced in size by grinding or micropulverizing to facilitate melting.

The thickness of the photoconductor and arsenic trisulfide layers is not at all critical. In general, the arsenic trisulfide interlayer may vary from about $\frac{1}{10}$ micron to about 3 microns while the photoconductive insulating material may vary from about 10 microns to about 200 microns.

What is claimed is:

1. A xerographic plate comprising a conductive backing having thereon a layer of arsenic trisulfide from about $\frac{1}{10}$ to about 3 microns thick and a layer of a photoconductive insulating material from about 10 to about 200 microns thick on said arsenic trisulfide.

2. A xerographic plate comprising a support member, a layer of electrical conductive material, a layer of arsenic trisulfide from about $\frac{1}{10}$ to about 3 microns thick on said conductive material and a layer of a photo-

conductive insulating material from about 10 to about 200 microns thick on said arsenic trisulfide.

3. A xerographic plate comprising a conductive support member, a layer of arsenic trisulfide from about $\frac{1}{40}$ to about 3 microns thick and a layer of vitreous selenium from about 10 to about 200 microns thick. 5

4. A xerographic plate comprising a conductive support member, a layer of arsenic trisulfide from about $\frac{1}{40}$ to about 3 microns thick, a layer of vitreous selenium on said arsenic trisulfide and a protective insulating coating on said selenium from about 10 to about 200 microns thick. 10

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,901,349

August 25, 1959

Roland M. Schaffert et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 18, for "trifluoride" read -- trisulfide --; column 3, line 37, after the numeral "2" and before the comma, insert a closing parenthesis; column 4, line 26, for "ma.-second" read -- ma-second --; column 7, lines 10, 11, and 12, for "on said arsenic trisulfide and a protective insulating coating on said selenium from about 10 to about 200 microns thick." read -- from about 10 to about 200 microns thick on said arsenic trisulfide and a protective insulating coating on said selenium. --.

Signed and sealed this 30th day of August 1960.

(SEAL)

Attest:

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