

[54] **DUAL LAYERED PHOTORECEPTOR EMPLOYING SELENIUM SENSITIZER**

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[51] Int. Cl. **G03g 5/02**

[58] Field of Search **96/1.1, 1.2, 1.5; 252/501**

[56] **References Cited**

UNITED STATES PATENTS

3,037,861	6/1962	Hoegl et al.	96/1
3,159,483	12/1964	Behmenburg et al.	96/1
3,283,309	11/1966	Gaynor	96/1.1 X
3,291,600	12/1966	Nicoll	96/1

3,312,547	4/1967	Levy	96/1.5
3,338,710	8/1967	Goffe	96/1.1
3,394,001	7/1968	Makino	96/1.5
3,443,937	5/1969	Ewing	96/1.1
3,573,906	4/1971	Goffe	96/1.8

OTHER PUBLICATIONS

Dessaver & Clark, Xerography and Related Processes, 1965, pp. 96-97.

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[57] **ABSTRACT**

An electrophotographic photosensitive plate is composed of an electrically conducting plate having adjacent thereto a vitreous selenium layer, said layer having adjacent thereto a layer of organic photoconductive insulating material which is substantially non-light sensitive in the visible ray region.

13 Claims, 2 Drawing Figures

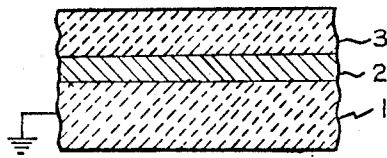


FIG. 1

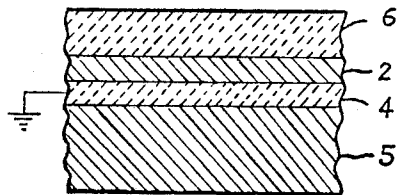


FIG. 2

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DUAL LAYERED PHOTORECEPTOR EMPLOYING SELENIUM SENSITIZER

This invention relates to an electrophotographic photosensitive plate, and particularly relates to a reusable photosensitive plate. More particularly, it relates to an electrophotographic photosensitive plate which is flexible and colored transparent.

In the prior art of electrophotography, it is common to form an electrostatic latent image on an electrically conducting body having a photoconductive insulating layer thereon. This purpose has been achieved by using a metallic member having a layer of vitreous selenium, or a paper member having a layer of dye-sensitized zinc oxide-binder dispersion. The metallic member having a very thick layer of vitreous selenium coated thereon is reusable but is not flexible. The thinner layer of vitreous selenium is more flexible but is poorer in photosensitivity. The paper member is flexible but is not as acceptable to reuse due to the fatigue effect of zinc oxide and the chemical degradation of dye-sensitizer (See Journal of Photographic Science, Vol. 10, page 57, 1962) by illuminated light.

Accordingly, an object of the present invention is to provide an electrophotographic photosensitive plate characterized by having a combination of a layer of organic photoconductive insulating material and a thin layer of vitreous selenium.

Another object of the present invention is to provide an electrophotographic photosensitive plate which is flexible and reusable.

A further object of the present invention is to provide an electrophotographic photosensitive plate which is flexible, reusable, and capable of light transmission.

These and other objects of the present invention will be apparent upon consideration of the following detailed description taken together accompanying drawings wherein,

FIG. 1 is a cross sectional view of an electrophotographic photosensitive plate according to the present invention.

FIG. 2 is a cross sectional view of another embodiment of an electrophotographic photosensitive plate according to the present invention.

The essence of the present invention is an electrophotographic photosensitive plate comprising, from the bottom up, an electrically conducting base plate, a vitreous selenium layer essentially thinner than 3μ and a layer of an organic photoconductive material which is substantially non-light sensitive in a visible ray from about 400 to 750 $m\mu$.

Referring to FIG. 1, an electrophotographic photosensitive plate according to the present invention comprises in order from the bottom up, an electrically conducting plate 1, a vitreous selenium layer 2 having a thickness ranging essentially from 0.05 to 3 microns and a layer 3 of an organic photoconductive insulating material which is substantially non-light sensitive in a range of visible ray from about 400 to 750 $m\mu$.

The said organic photoconductive insulating material is one which becomes substantially light sensitive in a range of visible ray from about 400 to 750 $m\mu$ when incorporated with any available and suitable sensitizer. Said electrophotographic photosensitive plate according to the present invention has a higher photosensitivity at a visible ray of about 400 to 750 $m\mu$ than that of

an electrophotographic photosensitive plate which includes a layer of organic photoconductive insulating material sensitized by an effective sensitizer with or without using a vitreous selenium layer. The use of sensitizer in said organic photoconductive material impairs the chemical stability of the resultant organic photoconductive insulating material under the irradiation of light in the visible ray region and prevents the resultant organic photoconductive insulating material from being reused repeatedly.

With regard to said electrically conducting plate 1 of FIG. 1, one can use any available and suitable conducting plate such as metal plate or paper.

It is preferable that said layer 3 of organic photoconductive insulating material of FIG. 1 is in a thickness from about 1 to 26 μ inclusive.

In a conventional electrophotographic photosensitive plate employing only a vitreous selenium layer coated on a metal base, a layer of vitreous selenium thinner than 10 μ has a lower surface potential and is not practically useful for electrophotographic photosensitive material to reproduce a satisfactory image thereon. Contrary to prior teachings, an electrophotographic photosensitive plate according to the present invention is satisfactorily light sensitive in a range of visible ray region and is capable of forming latent images of high potential and high contrast. Even when said vitreous selenium layer has a thickness less than 0.1 micron, an electrophotographic photosensitive plate according to the present invention can produce a visible image of high quality.

It has been reported by the Journal of Photographic Science, Vol. 7, Page 26 (1959) that vitreous selenium coating of a thickness less than 2.5 μ on clear glass base-plate are visually colored-transparent. At thicknesses about 0.2 μ or thinner the coating is of a yellowish color; at about 0.4 μ it is bright orange, at about 0.7 μ it is light red and becomes progressively deeper as the thickness of coating is increased, until at about 2.5 μ thickness it is a deeply ruby red. Further increase in thickness markedly reduces the light transmission to a very low value.

The thickness of vitreous selenium layer referred to herein is measured by a light interference method. The theory and the equipment for this method is disclosed in Japanese Patent Nos. 398,189 and 196,260. The equipment, so called micro-interferometer based on this method is commercially available under a trade name, MODEL MI from Olympus Optical Co., Ltd., Tokyo, Japan. During vacuum evaporation of selenium on aforesaid electrically conducting plate, a transparent glass plate is placed in a vacuum chamber and is coated with a vitreous selenium layer having the same thickness as that of vitreous selenium layer superposed on said electrically conducting plate. The thickness of vitreous selenium layer on the transparent glass plate is measured by said equipment and is defined as a thickness of vitreous selenium layer coated on said electrically conducting plate. The thickness so obtained is in a good agreement with that of the publication, Journal of Photographic Science, Vol. 7, Page 26 (1959).

The thickness of the organic photoconductive insulating layer referred to herein is measured by using a conventional mechanical thickness gauge such as a screw micrometer and a spring micrometer.

It has been also well known that a vitreous selenium layer has inherent photoconduction in the visible ray region, but its photosensitive range can be slightly changed with a variation in the thickness and the substrate temperature during evaporation and with types of incorporated additives such as, tellurium and arsenic. The electrophotographic photosensitive plate according to the present invention shows a spectral response very similar to that of the vitreous selenium layer.

In the electrophotographic photosensitive plate according to the present invention, the use of a vitreous selenium layer thicker than 3μ results in a reproduced image which is not entirely satisfactory. In addition, a vitreous selenium layer thicker than 3μ is brittle and makes it difficult to form a flexible electrophotographic photosensitive plate. A combination of vitreous selenium layer in a thickness of 3μ or less and flexible organic photoconductive insulating layer makes it possible to form a flexible organic photoconductive insulating layer makes it possible to form a flexible electrophotographic photosensitive plate in accordance with the present invention when it is applied to a flexible conducting plate such as aluminum foil and metalized polymer film.

A colored-transparent electrophotographic photosensitive plate can be obtained by using a combination of a vitreous selenium layer thinner than 1 micron and a substantially transparent layer of organic photoconductive insulating material which is substantially non-light sensitive in the range of visible ray region in accordance with the present invention, when the combination is applied to a substantially transparent conducting plate.

Referring to FIG. 2 reference character 4 is a substantially transparent conducting layer superposed on a transparent insulating substrate 5 such as a film of cellulose acetate, polystyrene, polyethylene and polyethylene terephthalate. A vitreous selenium layer 2 similar to that of FIG. 1 is interposed between said substantially transparent conducting layer 4 and a substantially transparent layer 6 of an organic photoconductive insulating material. Said substantially transparent conducting layer 4 can be obtained by using a thin layer of conducting material such as gold, silver, nickel, chromium, titanium and tin.

It is possible to employ any kind of organic photoconductive insulating material which is substantially non-light sensitive in the range of visible ray region. For example, the following substances are operable.

polyacenaphthylene

poly-N-vinyl carbazole

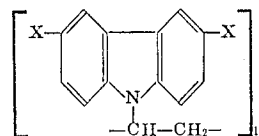
1,3-dibromo-poly-N-vinyl carbazole

poly-9-(4-pentenyl)-carbazole

poly-9-(5-hexyl)-carbazole

3-amino-carbazole in phenol resin These substances are known to be substantially transparent and to be adapted for practical electrophotographic photosensitive plate when they are incorporated homogeneously with at least one effective sensitizer such as Lewis acids and dyes.

It has been discovered according to the present invention that a more desirable electrophotographic photosensitive plate can be obtained by using a colorless mixture of polycarbonate resin and a photoconductive insulating polymer of the following chemical formula:



wherein, each X is, independently of the other, hydrogen or bromine and n is a positive integer. Such electrophotographic photosensitive plate is superior in flexibility, durability to mechanical wear, durability to the corona discharging atmosphere, dielectric strength, and quality of reproduced image. From the viewpoint of durability to mechanical wear, the best result is obtained when said mixture is in a composition consisting essentially of 10 to 50 weight percent of polycarbonate and 50 to 90 weight percent of said photoconductive insulating polymer shown by the chemical formula.

When the aforesaid organic photoconductive insulating materials are desired to be more flexible, one can add some plasticizers into said photoconductive insulating material. The preferable plasticizers are, for example, chlorinated diphenyl, epoxy resin and dioctyl phosphate.

It has been discovered according to the present invention that a copper iodide layer coated on an insulating substrate has a stronger adherence with the vitreous selenium layer. The stronger adherence between the vitreous selenium layer and the copper iodide layer results in higher flexibility and higher resistance to mechanical wear of the resultant electrophotographic photosensitive plate. When the copper iodide layer coated on a transparent insulating substrate is sufficiently thin to be substantially transparent, a substantially transparent electrophotographic photosensitive plate can be obtained by integrating a vitreous selenium layer in a thickness less than 1 micron and a substantially transparent layer of organic photoconductive insulating material in accordance with the present invention.

Said copper iodide layer can be prepared by a method described in the copending U.S. patent application, Ser. No. 769,680 filed on Oct. 22, 1968, now U.S. Pat. No. 3,677,816. There is no difficulty in finding a substantially transparent organic photoconductive insulating material which forms the layer 3 and has a strong adherence with the vitreous selenium layer. Any of the organic photoconductive insulating materials mentioned above has a sufficiently strong adherence with the vitreous selenium layer 2.

On any available and suitable insulating substrate such as polyethylene terephthalate film, cellulose acetate film or, glass plate, a layer of conducting material is superposed by any available and suitable method such as evaporation method, electroplating method or a laminating method. A vitreous selenium layer is integrated on said layer of conducting material by a vacuum evaporation method. The layer of an organic photoconductive insulating material is applied to the vitreous selenium layer by any available and suitable method such as a knife coating method or a roll coating method.

EXAMPLE 1

A polished aluminum plate of 10 cm \times 10 cm area is placed in a bell jar and a thin vitreous selenium layer is deposited on the aluminum plate 10^{-5} mm Hg by ordi-

nary vacuum evaporation method. The thickness of the vitreous selenium layer is 0.4μ . The aluminum plate is kept at a temperature of about 40°C during evaporation. The selenium coated aluminum plate is coated with the following organic solution by conventional knife method and dried with hot air at 50°C .

TABLE

	Parts by weight
polyacenaphthylene	100
chlorinated diphenyl	40
benzene	600

The dried layer of the coating is transparent and in thickness of 4μ . The resultant photosensitive plate which comprises three layers from the bottom up, aluminum based plate, vitreous selenium layer, and an organic top layer is stored in a dark place for a time period more than 24 hours. Then, the top surface of said photosensitive plate is sensitized to 450 static volt by negative corona ions in the dark and exposed to the image light of tungsten lamp of 26 lux.sec. Then, the conventional electrophotographic developer comprising iron carriers and positively charged toner particles is dispersed throughout said photosensitive plate by conventional magnetic brush development technique. The high contrast image of good quality is produced on said photosensitive plate.

The photosensitive plate is reusable and the photosensitivity shows no decrease after 3,000 times shuttle tests of a xerographic cycle including charging, image exposing, developing and cleaning processes.

EXAMPLE 2

A 150μ thick cellulose diacetate film is placed in a vacuum chamber and coated with thin copper film by using conventional vacuum evaporation method. The white light transmittance of the thin copper layer is 60 percent. The copper coated cellulose acetate is then immersed in a solution of 1 percent iodine in benzene so as to convert the thin copper layer to a transparent copper iodide layer. The white light transmittance and the surface electrical resistivity of the copper iodide layer are 87 percent and $10^5\Omega$, respectively.

The copper iodide coated cellulose diacetate film is again placed in the vacuum chamber and then is coated with a vitreous selenium layer by conventional vacuum evaporation method. The thickness and the white light transmittance of the vitreous selenium layer are about 50 percent to 0.1μ respectively.

The following organic solution is applied to the vitreous selenium layer by using conventional knife method and is dried.

TABLE 2

	Parts by weight
poly-N-vinyl carbazole	100
chlorinated diphenyl	60
toluene	800

The thickness of the dried coating is 5μ .

The resultant electrophotographic photosensitive film of four layers which is flexible and colored-transparent, is placed at a negative corona ion atmosphere in the dark in order to sensitize the surface of said organic layer. Then an image light of 10 lux. is applied

thereon for 2 seconds. The latent image produced is developed in the dark by immersing the film of four layers for 4 seconds into a liquid developer which consists of positively charged graphite particles, cobalt naphthenate, and trifluoro-trichloroethane.

The image reproduced is very fine and the resolution is 100 lines/mm or more. The image is able to be projected into a large picture by conventional slide projector.

EXAMPLE 3

Electrophotographic photosensitive plates are prepared by integrating, from the bottom up, 0.4 mm thick aluminum base plate, thin vitreous selenium layer and transparent organic layer of the following chemical formulation:

TABLE 3

	Parts by weight
poly-N-vinylcarbazole	100
polycarbonate	30

The preparation method of above electrophotographic photosensitive plates are essentially similar to that of Example 1.

Two kinds of electrophotographic photosensitive plates are prepared; (1) the thickness of vitreous selenium layer is 0.3μ and the thickness of transparent organic layer is 5, 10, 14, 18 and 26μ and (2) the thickness of transparent organic layer is 10μ and the thickness of vitreous selenium layer is 0.15, 0.3, 0.7, 1.0 and 2.0μ . The imaging test indicates that all of these plates reproduce entirely satisfactory images.

EXAMPLE 4

Three layered film which comprises from the bottom up, 125μ thick polyethylene terephthalate, 500A thick copper iodide layer and 0.3μ thick vitreous selenium layer is prepared by same method as described in Example 3. Then, the following solution is applied onto the vitreous selenium surface and dried.

TABLE 5

	Parts by weight
Brominated-N-vinyl carbazole polymer	100
polycarbonate	30
dichloroethane	300
monochlorobenzene	900

The method of synthesis of brominated poly-N-vinyl carbazole is carried out according to U.S. Pat. No. 3,421,891.

The electrophotographic imaging process as described in Example 1 is then applied to the resultant four layered sample. The fine image is developed with tungsten light of 40 lux.sec. The sample is able to be reused for electrophotographic imaging test repeated more than 20,000 times.

For comparison between the films within and without the scope of the present invention, the above three layered film without a selenium layer is tested with the electrophotographic imaging process. The testing result clearly indicates that the three layered film without the scope of the invention is substantially non-light sensitive and shows a poor quality image even when exposed to a high illumination of 60,00 lux.sec.

EXAMPLE 5

Vitreous selenium layer of 0.3μ thick is superposed on a polished aluminum base plate of 0.4 mm thick by a conventional evaporation method. Then, the following solution of Table 6 is applied to the vitreous selenium layer and dried to form an organic top layer.

TABLE 6

	Parts by weight
poly-N-vinyl carbazole	100
polycarbonate	30
dichloroethane	300
monochlorobenzene	900

The thickness of the organic top layer is 9μ .

These samples are subjected to same electrophotographic imaging process as described in Example 1. A fine image is obtained by illumination of tungsten light of $40\text{ lux}\cdot\text{sec}$.

For the comparison of the photosensitive plates within and without the scope of the invention, the solution of Table 7 is applied to the vitreous selenium layer in a 0.3μ thickness coated on a polished aluminum plate and dried to form an organic top layer. The dried top layer is in a thickness of about 9μ .

TABLE 7

	Parts by weight
poly-N-vinyl carbazole	100
polycarbonate	30
2-methoxy styryl-3-phenyl benzopyrilium perchlorate	0.3
dichloroethane	300
monochlorobenzene	900

The solution of Table 7, which includes 2-p-methoxy styryl-3-phenyl benzopyrilium perchlorate to form an organic top layer sensitive to light in a visible range, is without the scope of the invention. The sample is subjected to the same electrophotographic imaging process as described in Example 1. The test result indicates that the reproduced image is vague and low in density and contrast.

EXAMPLE 6

Poly-9-(4-pentenyl)-carbazole is prepared in a manner described in Examples 1 and 3 of British Patent Specification 1,075,626. The melted polymer at 190°C is applied to a smooth glass substrate to form a thin film about 10μ thick (when dried). Then the film coated glass is placed in a vacuum chamber at room temperature and evacuated to 10^{-5} mm Hg in order to superpose, in the order, thin vitreous selenium layer and aluminum layer thereon.

The thickness of the superposed vitreous selenium layer and the aluminum layer are 0.5μ and 10μ , respectively. The glass substrate is separated from the layer of poly-9-(4-pentenyl)-carbazole.

The surface of poly-9-(4-pentenyl)-carbazole is supplied with a voltage of 400 volts negative corona in the dark, and then illuminated with an image light by tungsten source. The illuminance is $50\text{ lux}\cdot\text{sec}$. Latent image produced thereon is developed with conventional cascade development technique, in which the used developer consists of positively charged toner particles and glass bead carriers.

The reproduced image is excellent and the electrophotographic photosensitive plate are reusable in xerographic cycle test more than two thousand times.

EXAMPLE 7

3-amino-carbazole is synthesized according to the British Patent Specification 947,488. A mixture of 1 weight part of the resultant 3-amino-carbazole and 1 weight part of a phenolic resin is prepared by using monochlorobenzene as a solvent. The colorless transparent mixture is then applied to a thin vitreous selenium layer superposed on an aluminum plate similar to that of Example 1 by using a conventional knife method to form an organic top layer. The dried organic top layer is 4μ in thickness.

The resultant electrophotographic photosensitive plate is subjected to the same electrophotographic imaging test as described in Example 6. The fine image of high contrast is obtained by image light illumination of $30\text{ lux}\cdot\text{sec}$.

EXAMPLE 8

3,6-dibromo-9-vinylcarbazole polymer is prepared by the method described in U.S. Pat. No. 3,421,891.

A solution mixture of 100 weight parts of said polymer and 40 weight parts of polycarbonate is prepared by using 1,100 weight parts of dichloroethane.

The solution is then applied to a thin vitreous selenium layer superposed on an aluminum plate similar to that of Example 1 by using a conventional knife method to form a transparent organic top layer. The dried organic top layer is 8μ in thickness.

The resultant electrophotographic photosensitive plate is subjected to the same electrophotographic imaging test as described in Example 6. A fine image of high contrast is obtained by image light illumination of $30\text{ lux}\cdot\text{sec}$.

EXAMPLE 9

Copolymer of N-vinyl carbazole and methylacrylate is obtained by the method described in U.S. Pat. No. 3,122,453. A solution mixture of 10 weight parts of said copolymer and 2 weight parts of chlorinated diphenyl is prepared by using, as a solvent, 100 weight parts of methylene chloride. The solution is then applied to the surface of a thin vitreous selenium layer superposed on an aluminum plate similar to that of Example 1 by using a conventional knife method. The dried organic top layer is 5μ in thickness.

The resultant electrophotographic photosensitive plate is subjected to an electrophotographic imaging test the same as described in Example 6. A fine image is obtained by image light illumination of $60\text{ to }80\text{ lux}\cdot\text{sec}$.

EXAMPLE 10

A polymer of 9-vinylanthracene is obtained according to the process described on line 5 to 10, Page 2 of British Patent Specification 1,101,391. A solution mixture of 10 weight parts of said polymer and 3 weight parts of chlorinated diphenyl is prepared by using, as a solvent, 100 weight parts of benzene. The solution is then applied to the surface of a thin vitreous selenium layer superposed on an aluminum plate similar to that of Example 1 by using a conventional knife method. The dried organic to layer is 3μ in thickness.

The resultant electrophotographic photosensitive plate is subjected to an electrophotographic imaging test the same as described in Example 6. A fine image is obtained by image light illumination of $80\text{ lux}\cdot\text{sec}$.

What is claimed is:

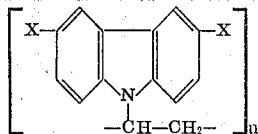
1. An electrophotographic plate for producing an electrostatic latent image on the top layer thereof which comprises from the bottom up:

- a. a conductive substrate;
- b. a layer of vitreous selenium having a thickness of from 0.05 to 3 microns;
- c. a top layer comprising a member selected from the group consisting of poly-N-vinyl-carbazole, polyacenaphthylene, poly-9(4-pentenyl) carbazole, poly-9-(5-hexyl)-carbazole, poly-3-aminocarbazole, brominated poly-N-vinyl carbazole, copolymers of N-vinylcarbazole and methylacrylate and poly-9-vinylanthracene;

said top layer being substantially visible ray transmissive and substantially non-light sensitive in the visible range in the absence of a sensitizer;

the sensitizer for said top layer consisting essentially of vitreous selenium layer b.

2. An electrophotographic plate according to claim 1 wherein said top layer comprises a compound of the formula:



wherein each X independently is hydrogen or bromine and n is a positive integer.

3. An electrophotographic plate according to claim 1, said top layer consisting essentially of a brominated poly-N-vinylcarbazole.

4. A reusable electrophotographic plate according to

claim 1 wherein said top layer consists essentially of polyacenaphthylene.

5. A reusable electrophotographic plate according to claim 1 wherein said top layer consists essentially of poly-9-(4-pentenyl)-carbazole.

6. An electrophotographic plate according to claim 1, wherein said top layer consists essentially of poly-9-(5-hexyl)-carbazole.

7. An electrophotographic plate according to claim 1, wherein said top layer consists essentially of poly-3-aminocarbazole.

8. An electrophotographic plate according to claim 1, wherein said top layer consists essentially of poly-N-vinylcarbazole.

9. An electrophotographic plate according to claim 1, wherein said top layer consists essentially of a copolymer of N-vinylcarbazole and methylacrylate.

10. An electrophotographic plate according to claim 1, wherein said top layer consists essentially of poly-9-vinylanthracene.

11. An electrophotographic plate according to claim 2, wherein said top layer further contains polycarbonate resin in an amount of 10 to 50 weight percent to the total amount of said top layer member and said polycarbonate resin.

12. An electrophotographic plate according to claim 3, wherein said top layer further contains polycarbonate resin in an amount of 10 to 50 weight percent to the total amount of said top layer member and said polycarbonate resin.

13. An electrophotographic plate according to claim 8, wherein said top layer further contains polycarbonate resin in an amount of 10 to 50 weight percent to the total amount of said top layer member and said polycarbonate resin.

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Notice of Adverse Decision in Interference

In Interference No. 98,832, involving Patent No. 3,725,058, Y. Hayashi and M. Hasegawa, DUAL LAYERED PHOTORECEPTOR EMPLOYING SELENIUM SENSITIZER, final judgment adverse to the patentees was rendered May 29, 1980, as to claim 1.

[Official Gazette November 18, 1980.]