May 6, 1958 P. K. WEIMER 2,833,675

METHOD OF IMPORTING RED RESPONSE TO A PHOTOCONDUCTIVE TARGET FOR A PICKUP TUBE

Filed Oct. 1, 1953 2 Sheets-Sheet 1

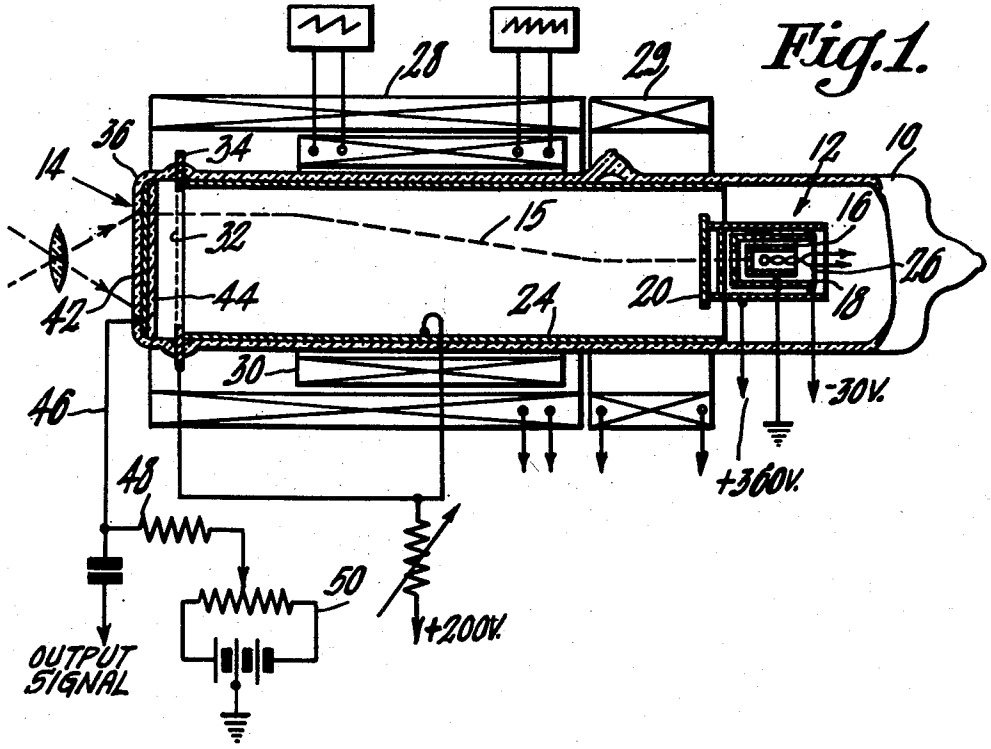



Fig. 1.

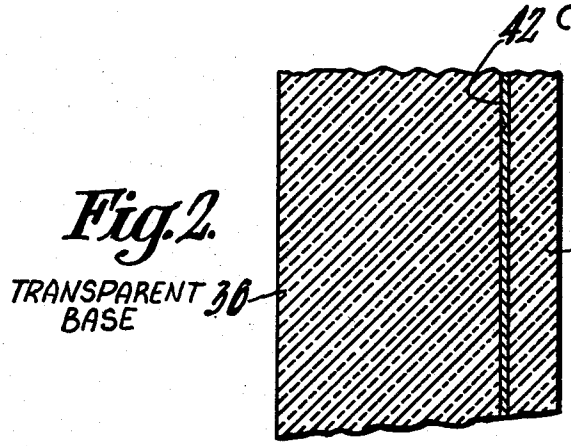



Fig. 2.

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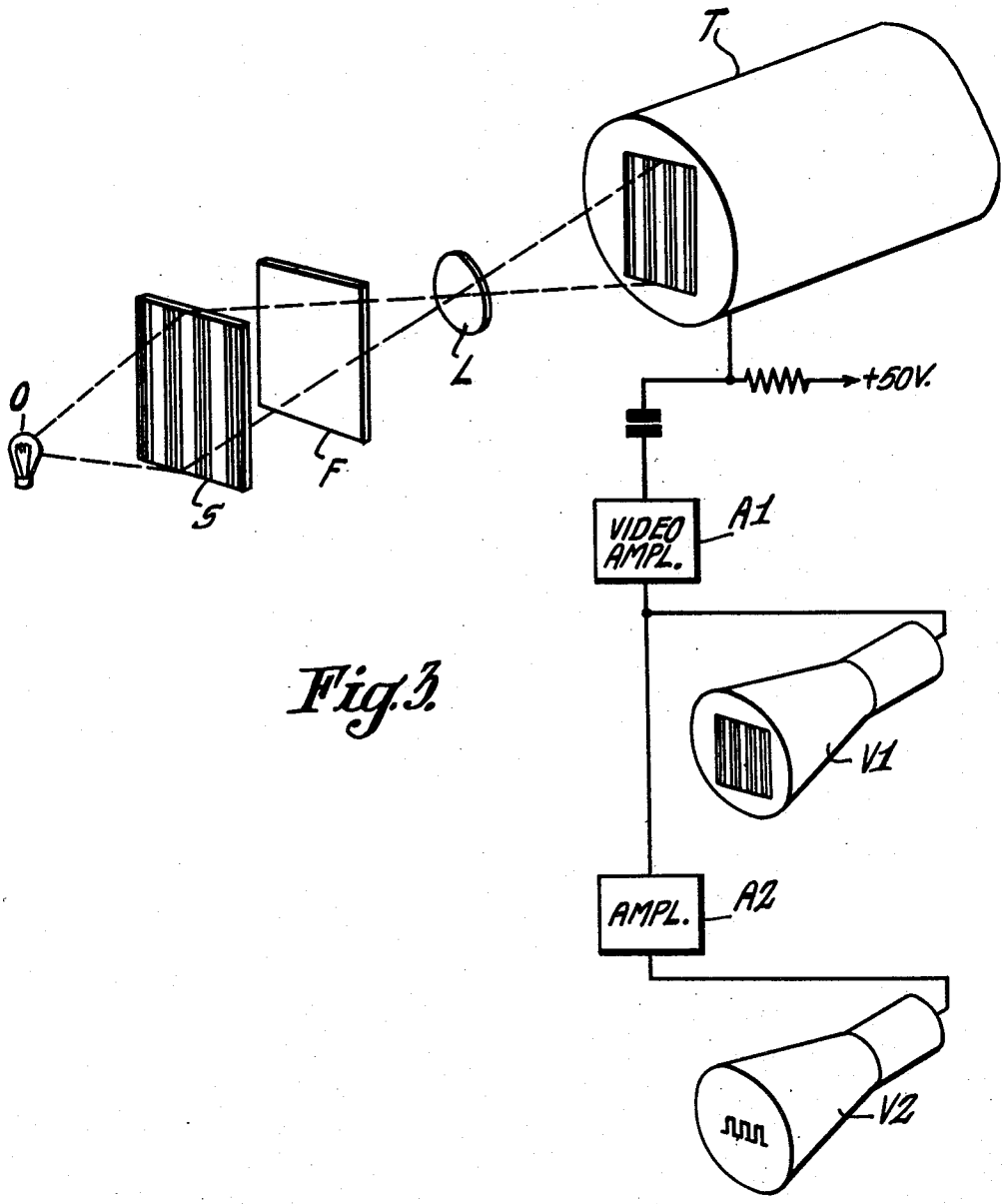



Fig. 3.

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2,833,675

# METHOD OF IMPARTING RED RESPONSE TO A PHOTOCONDUCTIVE TARGET FOR A PICKUP TUBE

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6 Claims. (Cl. 117—201)

This invention relates to photoconductive materials, and particularly to photoconductive materials suitable for use in electron discharge devices.

Although the photoconductive materials of the present invention may be used in many applications such as photo-tubes, xerography, or pickup and camera tubes, it will be principally described here as applied to a photoconductive pickup tube for television use.

A photoconductive pickup tube is one having a target formed with a supporting transparent sheet portion, which is first coated with a transparent conductive film or signal plate and then, secondly, with a layer of known photoconductive material over and in contact with the conductive film. This target electrode is mounted within an evacuated envelope with the photoconductive coating facing an electron gun structure, including a cathode, which produces an electron beam substantially normal to the target surface. Either electrostatic fields or electromagnetic fields can be used to cause the electron beam to scan, in closely spaced parallel lines, over the surface of the photoconductive target layer. The beam electrons are slowed down so that they approach the target surface with low energies. Electrons from the beam are deposited on the photoconductive surface to drive the surface to substantially cathode potential. When the photoconductive surface is at this potential, the remaining portion of the electron beam is reflected back toward the gun. There is applied to the conductive signal plate of the target a potential that is several volts different from the cathode potential established on the photoconductive surface. In this manner, then, a difference of potential is established between the two surfaces of the photoconductive film.

Due to the photoconductive properties of the target material used, when light is focused upon the photoconductive film, a current flow will take place through the film in the illuminated areas and will change these areas toward the potential of the conductive film. Areas of the target not illuminated by the light will have little or no current flow, depending upon the resistivity of the photoconductive material in the dark, and will thus remain at the cathode potential established by the beam. The electron beam, upon scanning over the target areas illuminated by light, will deposit electrons on the photoconductive surface and thus return the illuminated target areas to cathode potential. Since the signal plate is capacitively coupled with the scanned surface of the target, the instantaneous charging of the target by the beam to cathode potential will be evidenced by a voltage change in the circuit of the signal plate. This voltage change becomes the output signal of the tube.

A photoconductive material, in order to be effectively used for a pickup tube target, must exhibit sufficient dark resistivity to give storage during tube operation, because the potentials established on the photoconductive surface areas of the target by the electron beam must be maintained in the unilluminated target areas.



If the photoconductive target material has low dark resistivity, the dark current through the material will discharge the target in the dark areas, thus masking the light output signal derived from the illuminated areas.

One such photoconductive material which has been successfully used in pickup tubes is amorphous selenium. Such use of amorphous selenium is fully described in my co-pending application Serial No. 78,687, filed February 28, 1949, which is now U. S. Patent 2,654,853, issued October 6, 1953. Amorphous selenium, as a photoconductive material, has good sensitivity for phototube applications and has satisfactory resistivity in the dark.

However, because amorphous selenium has good blue and green spectral response and practically none to red, it is unsuitable for use in many devices where balanced color sensitivity is required. For instance, photoconductive pickup tubes used in color television require a target material which has good color response to each of the primary colors.

Crystalline selenium has good overall color response but also has low dark resistivity, which makes it unsuitable for use by itself in photoconductive pickup tubes. Other target materials may be responsive to red, but in general each material is somewhat insensitive to one or more colors.

Some photoconductive targets for use in pickup tubes have been made which have reasonably good overall color response. However, most of these have been multi-layered targets which are not as sensitive as may be desired. Further, multi-layered targets are more complicated to form, particularly when the target is formed on the endplate of a small pickup tube.

In working with amorphous selenium targets, I have found that changes in the photoconductive properties of selenium may be brought about by heating the selenium. For example, if selenium is evaporated onto a supporting glass plate maintained at a temperature below about 50° C., the deposited selenium is amorphous in character. For temperatures above this, say between 65 and 90° C., amorphous selenium changes to the crystalline form. Thus, I have made amorphous selenium targets which contain minute quantities of crystalline selenium, by evaporating selenium onto a glass plate which is kept at a temperature higher than that at which the amorphous form alone will be formed. The structure formed in this manner does have a red response, which is not present in amorphous selenium. However, due to the inherent instability of amorphous selenium at temperatures above 50° C., it is difficult to control the growth of crystals so that they do not extend as in a chain through the photoconductive layer and thus form spots which are conducting even in the dark. One reason why it is difficult to prevent the formation of conducting spots is that as soon as a minute quantity of selenium is deposited on to a heated base plate, crystals begin to form. Then, as other quantities of selenium are evaporated onto the heated base plate in succession, crystals begin to form in these later deposits, but also the growth of crystals continues from those crystals which were formed previously because they have been heating for a longer time. Thus, the conditions are favorable for the growth of large crystals which form a conductive path right through the selenium layer. This is undesirable in a pick-up tube.

Accordingly, a principal object of the present invention is to provide an improved photoconductive material.

Another object of the present invention is to provide a photoconductive material which is responsive to all the primary colors.

A further object of the present invention is to provide

a photoconductive material having improved and balanced sensitivity to the primary colors.

A more specific object of the present invention is to provide an improved pickup or camera tube having a photoconductive target responsive to all primary colors and having improved sensitivity.

Yet another object of the present invention is to provide an improved single layer photoconductive target which has improved overall color sensitivity and high dark resistivity.

Another object is to provide a method of heat treating a selenium pickup tube target, which method provides a target having improved overall color response and which discourages the formation of undesirable conducting spots.

The above and related objects are achieved in accordance with the present invention by depositing a layer of amorphous selenium on a cool surface and then heat treating the photoconductive layer under controlled conditions as to temperature and time to partially convert the amorphous selenium to a crystalline form of selenium.

Photoconductive targets made in accordance with the present invention have been found to have nearly uniform response to each of the primary colors and have increased sensitivity as compared to multi-layered targets. Further, targets made in accordance with the present invention are simpler to form within a camera tube than are multilayer targets which respond to all the primary colors of light.

Referring to the accompanying drawings:

Fig. 1 is a sectional view of a camera or pickup tube having a target incorporating the present invention;

Figure 2 is a sectional view of the target of the tube of Fig. 1, and

Fig. 3 is a schematic representation of a test circuit for observing the photoconductive response of the tube of Fig. 1.

Figure 1 discloses a photoconductive pickup tube having an evacuated envelope **10**, within which is positioned an electron gun structure **12** and a target electrode **14**. The electron gun **12** provides an electron beam **15** which is scanned over the surface of the target **14**. The electron gun is of conventional design and consists essentially of a cathode electrode **16**, a control grid **18** and accelerating electrodes **20** and **24**. Electrode **24** may be a conducting wall coating. Electrodes **20** and **24** also provide partial focusing of beam **15**. Cathode **16** is essentially a tubular electrode closed at one end with the closed end facing the target electrode **14**. The closed cathode end is coated with thermionic emitting material, which is heated preferably by a non-inductive heater coil **26** to provide an electron emission. This emission is formed, in a well known manner, by electrodes **18** and **20**, into the electron beam **15**.

The electrons of beam **15** are magnetically focused for a well defined point on the surface of target electrode **14** by a magnetic coil **28**, which encloses the tube envelope **10**, as is shown. Smaller alignment coils **29** may also be placed adjacent to the tube walls for the purpose of compensating for mechanical misalignment of the electron gun or target. A yoke structure, indicated at **30**, comprises essentially two pairs of coils, with the coils of each pair connected in series respectively to sources of saw-tooth voltages, for providing line and frame scansion of beam **15** over the surface of target **14**. Such a deflection system is well known, and does not constitute a part of this invention. During tube operation, voltages are applied to the several electrodes as is indicated. These voltages represent appropriate values for tube operation. However, operation of the tube need not be limited to these values.

Accelerating and focusing electrode **24** may comprise a conductive coating on the inner wall of the tube envelope. The conductive coating **24** extends to a point closely adjacent to target electrode **14**. Conductively connected to coating **24** is a fine mesh screen **32**, which is mounted in the tube envelope across the opening of a ring **34** sealed in the tube envelope **10**.

Target electrode **14** comprises essentially a supporting insulating transparent base member **36**, such as glass, for example, which in the tube of Figure 1 is a flat end wall portion or face plate of envelope **10**. The target supporting base member may also consist of a separate plate mounted within envelope **10** and closely spaced from the tube end **36**. The glass member **36** is coated on its surface facing the electron gun **12** with a transparent conductive film or signal plate **42**. Such a conductive film may be formed from evaporated metal or of such material as stannic oxide to provide a transparent conductive film. Conductive film **42** is coated with a thin layer **44** of photoconductive material, which according to this invention is amorphous selenium heat treated in a manner to be later described.

During tube operation, appropriate voltages are applied to the several electrodes within the tube. The electron beam **15**, which is formed thereby, is scanned over the surface of the photoconductive material **44**. Beam **15** approaches the surface of the target **14** at substantially zero, or gun cathode, potential. Electrons are deposited on the scanned surface of the photoconductive layer **44**, and drive the surface down toward an equilibrium potential, which approaches cathode or ground potential. The conductive signal plate **42** is connected by a lead **46** through a load resistance **48** to a source of potential **50**, to establish on signal plate **42** a potential from 10 to 20 volts positive, relative to the equilibrium potential of the scanned surface of the photoconductive layer **44**. When light is focused upon the target **14**, the illuminated portions of the target become conductive, and because of the potential difference across the photoconductive layer **44**, a current flows in these areas between the positive signal plate **42** and the scanned surface of the photoconductive layer **44**. This flow of current discharges the scanned surface of the photoconductive layer **44** towards the potential of the signal plate **42**. As the scanning beam **15** passes over the discharged areas of the screen, it tends to rapidly drive these areas toward equilibrium or ground potential. This almost instantaneous charging of a discharged area of the target toward the equilibrium potential provides corresponding potential changes across the load resistance **48**, as signal plate **42** is capacitively coupled to the scanned surface of the photoconductive layer **44**. The changes in potential across the load resistance **48** are picked up and amplified, in a well known manner, to provide the video or output signal of the pickup tube.

Figure 2 shows an enlarged view of the target of Figure 1 formed in accordance with my invention. The conductive film **42** may be formed by any of the methods well known to those skilled in the art, for example by pyrolitic deposition from a mixture of air or oxygen and the vapors of stannic chloride and methanol. On the exposed surface of the conductive film **42** is formed the layer **44** of amorphous selenium by evaporation in vacuum and in a manner discussed in my above cited patent. It is important that the selenium be evaporated on a cool surface, for example, a temperature below 50° C., in order to provide a layer of selenium in the amorphous form only. The layer **44** of selenium is formed with a thickness preferably of about 1–10 microns.

After the layer **44** of selenium is deposited on the conductive film **42** the selenium is subjected to controlled heat treatment to change it into the form which will give the desired response characteristics. This may be done by dipping the target end of the finished tube in a hot liquid such as water and holding it there for a time. This method of heat treatment is preferable to oven baking because it is susceptible to better heat control. The tube

may then be removed from the hot liquid and cooled by dipping it in a cooler bath, say at below 50° C.

To determine whether sufficient heat treatment has been applied to change the characteristics of the target to give the proper response, the cooled tube may be given a photoconductivity test. A block diagram of a suitable test circuit is illustrated in Figure 3. A light pattern, such as a series of parallel bars, is focused on the face of a pickup tube T processed in the manner just described, as by means of a lantern slide S, illuminated by a light source O, and followed by a red filter F and lens system L. The signal developed on the signal plate of the target passes through a video amplifier $A_1$ and is received by a kinescope $V_1$ where the target image is reproduced for visual observation. The signal may simultaneously be fed through a second amplifier $A_2$ to a cathode-ray oscilloscope $V_2$ for quantitative measurements of photoconductivity. If the heat treatment has produced a target responsive to red light, the image will appear on the kinescope face as a bright pattern of bars against a dark background as shown in Figure 3. The oscilloscope trace will have the shape of a rectangular wave, the positive regions corresponding to the light portions of the image and the negative regions corresponding to the dark portions. Thus, the sensitivity can be measured on the oscilloscope by measuring the height of the trace.

If greater sensitivity is desired, the tube can be subjected to further heat treatment in accordance with the process described. However, if too much heat treatment is applied, objectionable conducting spots will form. To prevent the formation of large spots, the amplifier $A_1$ is operated at a gain considerably higher than normal in order to detect on the kinescope any spots which might form. If the condition is reached where small conducting spots become visible at this higher gain than the heat treatment is discontinued even though maximum sensitivity has not been achieved.

Instead of observing only the red response, one may desire to test the overall color response of the target. This may be done by passing the light through separate red, green and blue filters to obtain on the target face a series of bars corresponding separately to red, green and blue light. The relative brightness of the bars on the kinescope face and the relative heights of the rectangles of the oscilloscope trace is then determinative of the relative color response.

Thus be heat treating the tube target in steps, with intermediate testing of red response and sensitivity, and scrutiny for conducting spots, a tube having the desired characteristics may be produced.

In carrying out this invention with targets having a thickness on the order of 1 to 10 microns, the amount of heat used for the treatment ranged from 15 minutes' total heating time at 80° C. to 1.5 minutes' total heating time at 100° C. These figures are given by way of illustration only, and suggest a range of starting points. The optimum treatment can best be ascertained by subjecting the tube to test in the manner described.

It will be observed that in the method of heat treatment of amorphous selenium in accordance with this invention, precautions are taken to hinder the rapid growth of large crystals. The selenium is deposited on a cool surface in the amorphous form and of a thickness corresponding to a completed target before the heat treatment begins. Then the entire amorphous selenium film is heated uniformly throughout so that each minute particle receives substantially the same amount of heat treatment. Additionally, the tube is tested to determine when the optimum processing has been achieved.

It is not clear as to the nature of the change in the selenium produced by the heat treatment. In accordance with my invention there are two theories which may explain the observed results. One is that a small fraction of the amorphous selenium is converted to crystalline selenium, and the isolated crystals distributed throughout the bulk of the amorphous selenium give the red sensitivity. The two crystalline forms of selenium, red and gray, are both known to be photosensitive to red light and either might tend to be formed as a result of heat treatment of the amorphous selenium. The second possible effect of the heat treatment is that a thin layer of crystalline selenium, either red or gray, may be formed on the boundary between the conductive film and the amorphous selenium. It has been demonstrated that a thin layer of metallic selenium deposited on the conductive film prior to the deposition of the amorphous selenium does greatly enhance the response of the amorphous selenium for pickup tube operation, and this is disclosed in my co-pending application, Serial No. 212,550, filed February 24, 1951, which is now U. S. Patent 2,687,484 issued August 24, 1954.

In the heat treatment method of enhancing red response described here, the dark current may be increased slightly but the increase in dark current is by no means as large as would be the case if the entire target were converted to metallic selenium. The target still retains its red color after the proper heat treatment, and it appears that the bulk of the selenium remains in the amorphous form.

What I claim is:

1. The method of forming a photoconductive layer on a supporting base member, said method comprising depositing a layer of amorphous selenium on said base member, said base member being maintained at a temperature below that at which crystalline selenium is formed, heating said layer uniformly at a temperature of the order of 80–100° C., and continuing the heating for a time within the approximate range of 15–1.5 minutes whereby the red response of said layer approaches a maximum.

2. The method of forming a photoconductive target for a pickup tube, said target to have a layer of selenium on a transparent conductive base member, said method comprising depositing a layer of amorphous selenium on said base member at a temperature below 50° C., heating said layer uniformly throughout its structure substantially in the temperature range of 80–100° C. to partially convert the selenium into crystalline selenium, and continuing the heating for a time within the range of 15–1.5 minutes whereby the red response of said selenium approaches a maximum.

3. The method of forming a red-sensitive target for a pickup tube, said method comprising depositing a layer of amorphous selenium of a thickness between 1–10 microns onto a transparent conductive base member at a temperature below 50° C., surrounding the target end of said pickup tube with a liquid heated to a temperature of 80–100° C. for a period of time of 15–1.5 minutes, cooling said target, and continuing the heating within said period until the red response of said target approaches a maximum.

4. The method of imparting a red response to a pickup tube having a target formed from amorphous selenium, said method comprising heating the target end of said tube to a temperature within the range of 80–100° C. to partially convert the amorphous selenium into crystalline selenium, and continuing the heating for a time within the range of 15–1.5 minutes until the red response approaches a maximum.

5. The method of imparting a red response to a pickup tube having a target formed from amorphous selenium, said method comprising heating the target uniformly throughout its structure to a temperature between 80–100° C., and continuing the heating within the time range of 15–1.5 minutes until the red response approaches a maximum.

6. The method of imparting a red response to a photo-

conductive pickup tube having a target formed from amorphous selenium, said method comprising dipping the target end of said tube into a container of liquid heated to a temperature on the order of 80–100° C. to uniformly heat said amorphous selenium, and continuing the heating for a period of time within the approximate range of 15–1.5 minutes until the red response approaches a maximum.



**References Cited** in the file of this patent

UNITED STATES PATENTS

| | | |
|---|---|---|
| 2,189,576 | Brunke | Feb. 6, 1940 |
| 2,199,104 | Johnson et al. | Apr. 30, 1940 |
| 2,438,923 | Kotterman | Apr. 6, 1948 |
| 2,622,219 | Schagen | Dec. 16, 1952 |
| 2,654,853 | Weimer | Oct. 6, 1953 |