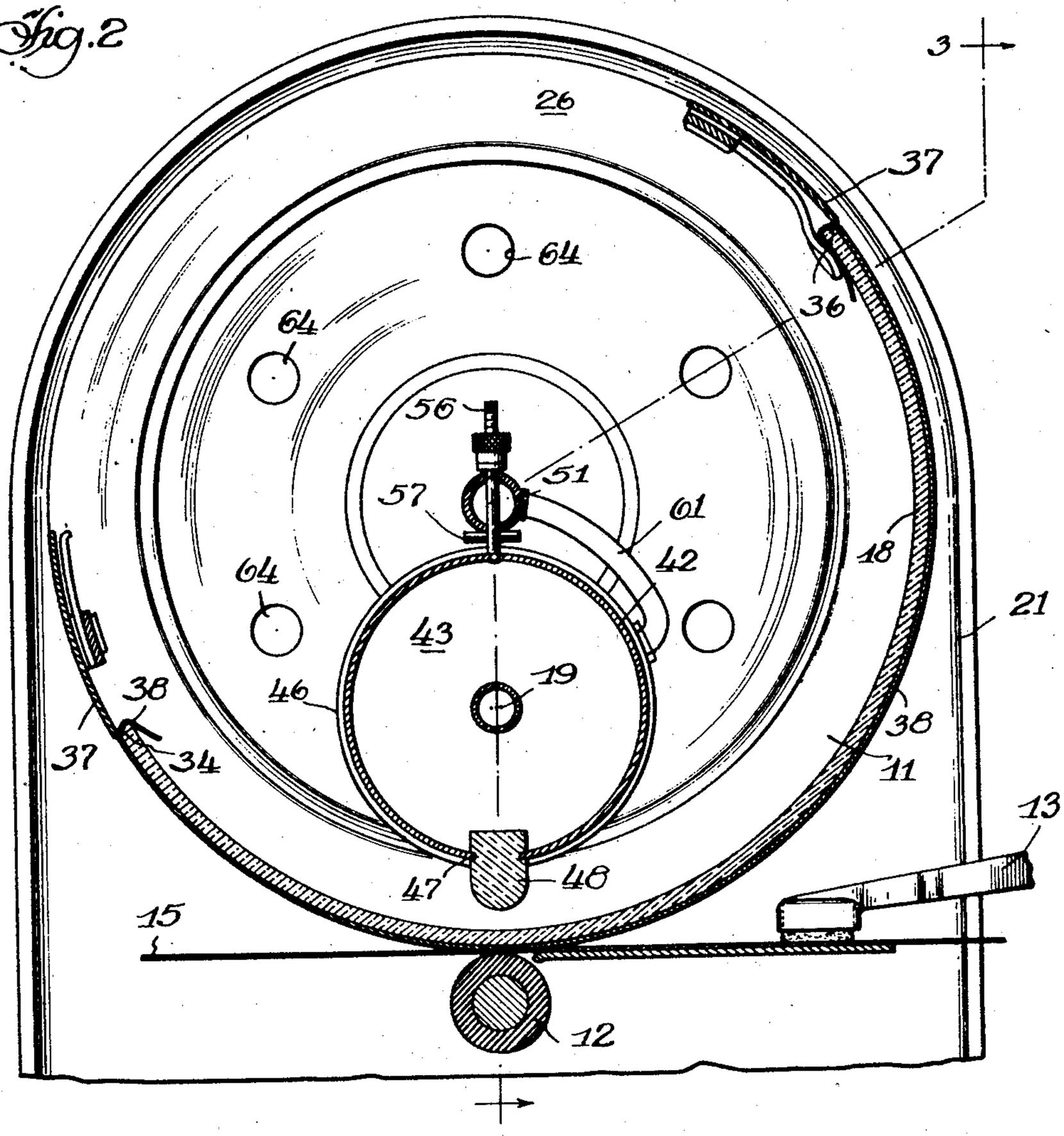
Sept. 16, 1947. T. R. COCHRAN 2,427,443

LIGHT-SENSITIVE LAYER AND PROCESSES OF MAKING AND EXPOSING IT

Filed June 4, 1943 2 Sheets-Sheet 1

Fig. 2



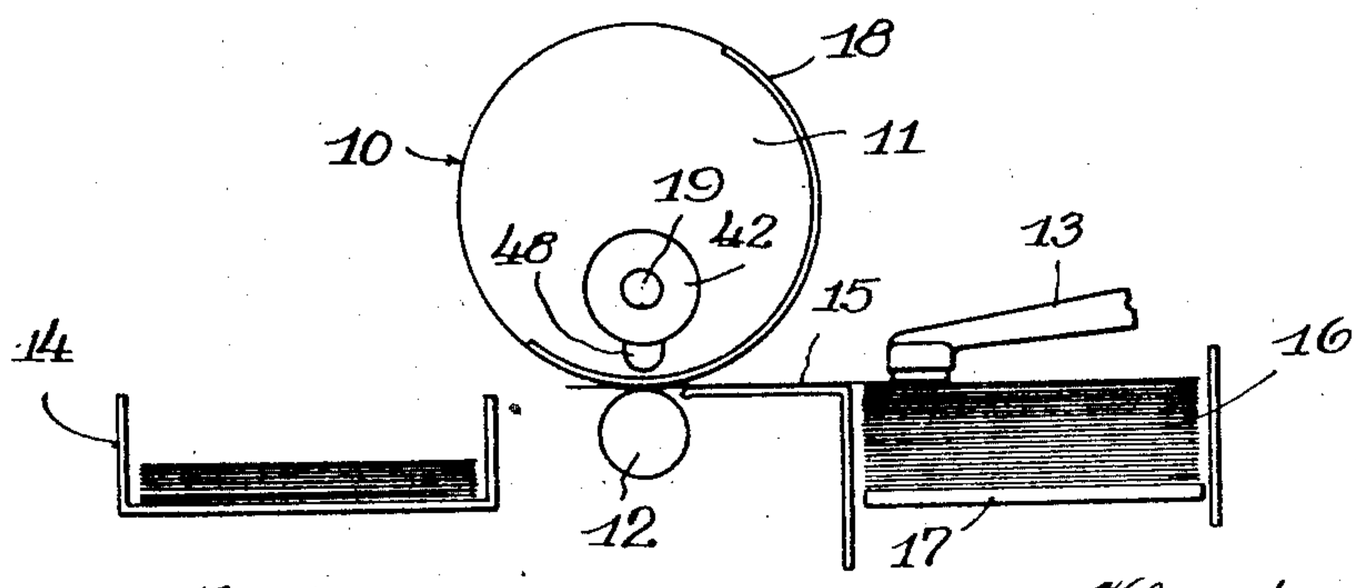


Fig. 1

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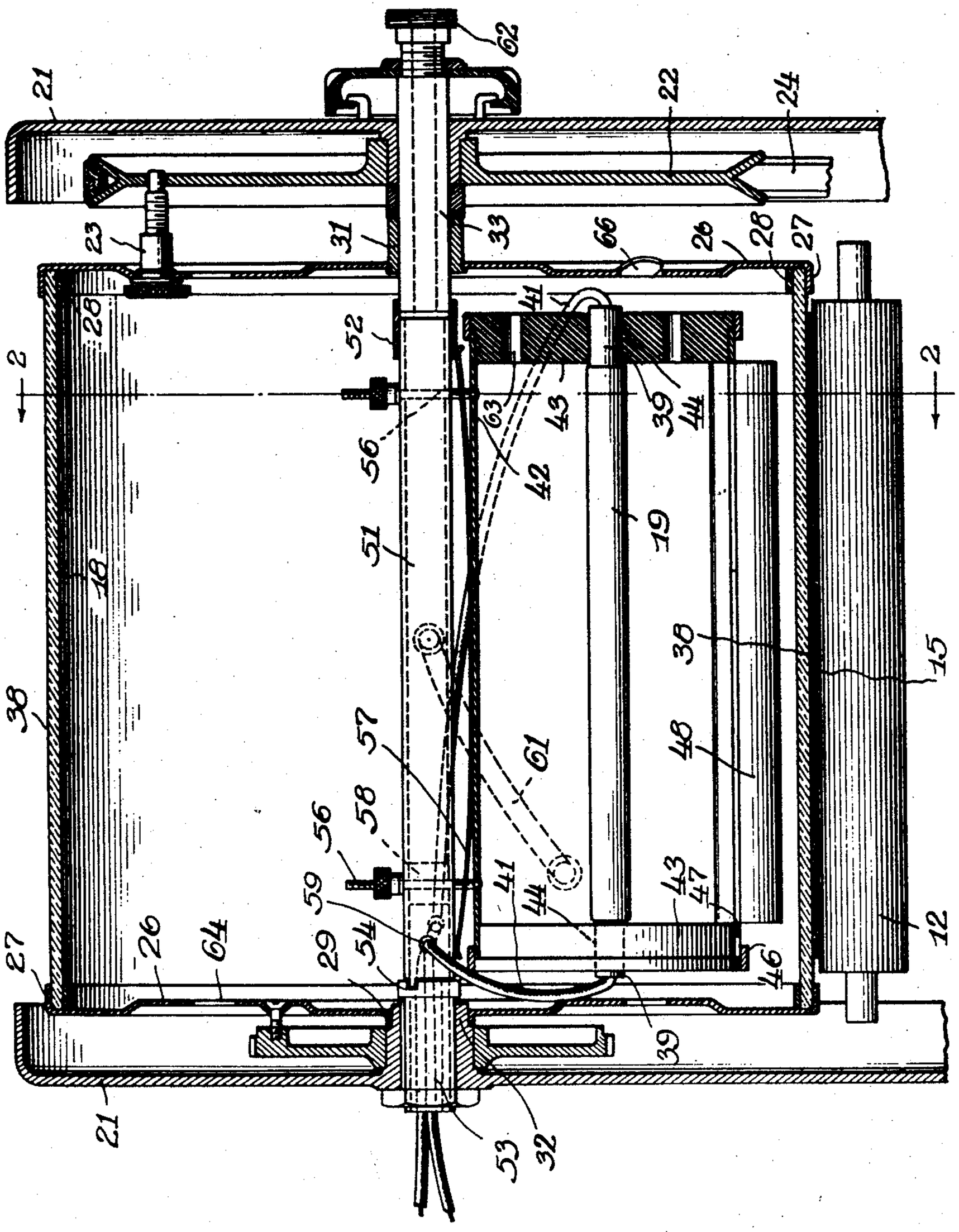

Fig. 3

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2,427,443

LIGHT-SENSITIVE LAYER AND PROCESSES OF MAKING AND EXPOSING IT

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Application June 4, 1943, Serial No. 489,597

8 Claims. (Cl. 95—7)

1

My invention relates to the duplication of copies and more particularly to the duplication by photochemical means of matter such as may be drawn or otherwise produced on a master sheet of the nature of a photographic film negative or a stencil sheet. It has for its principal object to provide a process of duplication which will produce clear, stable and accurate copies by simple photographic exposure of a suitable printing medium through the master, or negative, without the necessity of developing, fixing, washing or other manipulation of any kind, and which may be practiced in daylight or in ordinary artificial light without fogging or other damage to the prints.

Another object of the invention is to provide a process of duplication of the character designated which will be rapid and inexpensive, and which shall be clean and entirely dry.

Another object of my invention is to provide a printing medium comprising paper or other suitable substance coated, impregnated or otherwise charged with material which is sensitive to light waves in a band disposed in the low visible and high ultra-violet portion of the spectrum, which material is capable of definite, rapid and permanent color changes upon exposure to light waves in the specified band, but is insensitive or only slightly sensitive to daylight and ordinary artificial illumination.

My invention is predicated upon the fact that various organic compounds may be formed from certain metals which are not photo-sensitive to daylight but which are sensitive to light waves in a band which lies in the low visible spectrum close to and somewhat merging with the high ultra-violet. When exposed to such light waves, these compounds undergo chemical changes which are not reversible and which produce definite and permanent changes of color. The range of light waves which is useful for purposes of duplication in accordance with my invention lies between 3550 and 3750 A. U., and I have found that the most efficient wave length for the purpose is 3663 A. U., which is safely above that part of the ultra-violet spectrum which causes damage to eyes.

Light rich in rays in this duplicating range may be obtained from a number of sources, such as the carbon arc, although such light is usually also rich in the harmful ultra-violet rays. I prefer to use as a source of light the emanation from an electric lamp or generator of the well-known tubular type containing mercury and an inert gas. Such lamp, containing about one-half atmosphere of argon and sufficient mercury to sustain operation, has been constructed and is available. In this particular lamp over 40% of the total emanation lies in a band close to and including the desired light at 3663 A. U. Generators of this nature are satisfactory and efficient in operation and present no fire or electrical hazards, and the invention has been described in connection with such a device. However, it is to be understood that the invention is not limited to this particular equipment, any suitable source of the light waves being employed.

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The light-sensitive material is formed by treating various metals, or preferably the salts of metals, such as molybdenum, tungsten, strontium or vanadium, with certain organic acids, such as oxalic, acetic, tartaric, citric and the like. The sodium salts of molybdenum and tungsten when treated with oxalic acid form sodium molybdic oxalate and sodium tungstic oxalate, respectively. These give the best results, although the potassium and ammonium salts also produce color changes which yield legible copies. The oxalates are in general the better and more sensitive compounds, but the acetates, the tartrates, the citrates and compounds of other similar organic acids are suitable and may be used. Silver oxalate is also sensitive to light waves in the specified range, but its use is not indicated for duplicating purposes because this compound is explosive.

The light-sensitive material may be produced by separately dissolving the ingredients in hot water and then combining the hot aqueous solutions. By way of example, a sensitizing material satisfactory for general duplicating processes may be compounded as follows, in approximately the following proportions:

I

Sodium molybdate	grams	25
Sodium tungstate	do	25
Oxalic acid	do	50
Water	c. c.	100

The three solids may be dissolved in portions of the water and the solutions brought to boil. Upon combining these hot solutions a clear, yellowish solution is produced with a somewhat violent reaction. Upon cooling, this solution throws down a heavy, white crystalline precipitate which I believe consists of a mixture of sodium molybdic oxalate and sodium tungstic oxalate, which may be filtered off. The precipitate is removed from the filter, covered with 95% ethyl alcohol and shaken vigorously at intervals for a number of hours to remove the free oxalic acid. It may then be filtered from the al-

cohol and dried, either by means of ether or in the air. I have found, however, that the sensitiveness of the material is increased and that a superior print is produced by a shorter exposure if the alcoholic solution is evaporated to dryness and the residue washed with ether and dried. This procedure apparently recovers a part of the active material which is somewhat soluble in alcohol.

This active, light-sensitive material may be dissolved to form a solution for the sensitization of paper or other suitable material to provide print sheets for my process. Most simply, the material may be redissolved in hot water to the extent of about 14% and the solution used to impregnate paper. I prefer, however, to use a non-aqueous solution such as to render the material water-insoluble in the print sheet. I have found that the sensitizer is soluble generally in the hydrocarbons, such as benzol and toluol, in the ketones, such as acetone and the organic acetates, and in the polyhydric alcohols, such as the glycols and glycerol. Print sheets may be readily formed by impregnating sheets of paper with solutions of this nature, or with mixtures of such solutions, non-volatile portions of the solvent being readily absorbed in the paper fiber, or it may be applied in a surface coating in any suitable sizing such as nitrocellulose or gelatin.

The sensitizer may also be incorporated in the paper during the manufacture thereof. Thus, a sensitizing solution may be introduced into the pulp before formation of the paper web, as for example into the stuff box or the breast box, in quantities sufficient to sensitize the fiber content of the pulp and preferably with enough agitation to insure even distribution. The sensitizer may also be applied to the formed web at any stage, as by spraying the solution thereon, or it may be introduced into the sizing box. In applications of this sort, the sensitizing material, carried in a solvent such as benzol, is not affected by the pulp water present and the solution is preferentially accepted and absorbed by the fibers.

Print sheets sensitized with the material of Example I in the manner above described are colored blue by exposure to light of moderate intensity in the band described. The coloration takes place without other manipulation of any kind and remains fast without subsequent fixation or other treatment. The sheets first turn light blue, becoming progressively darker as the exposure continues and finally reach a permanent blue-black color which cannot be further deepened. The exposure time may be materially reduced by increasing the intensity of the source of light.

No very satisfactory measure of intensity of this light or emanation has been found, but the intensity and the exposure or printing time is generally dependent upon the energy input to the lamp. Thus a lamp efficiently generating printing light at an intensity satisfactory for duplicating purposes may require a loading of the order of 95 to 100 watts per inch of length. Exposed to such a light, print sheets made in accordance with the formula of Example I attain their final color at the end of approximately 90 seconds.

While the photo-sensitive material formed as above described will yield satisfactory prints when made from the pure salts, I have found that the results are considerably improved if commercial salts are used which contain traces of iron compounds from the kettles in which the salts are manufactured. Suitable iron salts, such as ferric

oxide or ferric or ferrous chloride, seem to act as a catalyst in the reaction by which my sensitive material is formed, and small amounts of such salts of the order of one-half of one per cent by weight may be advantageously added to the other ingredients.

The following examples will serve to further illustrate the composition of light-sensitive material suitable for the production of prints, the ingredients being in substantially the following proportions:

II

Sodium molybdate	grams	50
Oxalic acid	do	50
Water	c. c	100

This composition yields a sensitive material from which a print may be produced quite similar in character to that of Example I, differing therefrom principally in a lighter tone of the blue color. The final color is definitely a dark blue rather than a blue-black.

III

Strontium hydroxide	grams	42
Molybdic acid	do	25
Oxalic acid	do	67
Water	c. c	114

The sensitive compound produced from this composition yields an orchid color upon initial exposure which changes upon prolonged exposure to a deep purple.

IV

Molybdic acid	grams	25
Tungstic acid	do	25
Oxalic acid	do	50
Water	c. c	100

I have found that reasonably satisfactory prints may be secured from a sensitizer compounded directly from the metallic acids involved as illustrated in the above example. The molybdic and tungstic acids, suspended in hot water, are mixed with a hot aqueous solution of oxalic acid to form the sensitizer material. The resulting material produces a color change ranging from light blue to medium blue, and while it is not to be preferred for use in duplicating, it does not contain the complex sodium or potassium salts but only the more simple oxalates.

V

Sodium molybdate	grams	25
Vanadium oxide	do	25
Tartaric acid	do	100
Water	c. c	100

This composition will enable the production of prints which are pink upon initial exposure, turning upon longer exposure to a deep red.

Similar light-sensitive materials may be produced by the use of acetic acid or citric acid, but I do not consider the resulting prints to be as good, either from the standpoint of color or intensity, as those in the examples given above.

Exposure of the sensitized print sheets to the light through the negative may be effected in any convenient way to yield prints, as by means of an ordinary printing frame or in a printer of the continuous contact type, such as is commonly used for the making of blue-prints. Such printing methods are too slow for most duplication, and I have provided means for more rapid and efficient exposure of the print sheets in succession. The construction and operation of my device will appear from the following description, taken in connection with the draw-

ings which form a part of this specification and in which:

Fig. 1 is a schematic representation of a machine adapted for printing in accordance with my invention;

Fig. 2 is a longitudinal vertical section through the printing couple and associated parts of the machine illustrated in Fig. 1, taken substantially on the line 2—2 of Fig. 3, and

Fig. 3 is a transverse vertical section through the machine, taken substantially on the line 3—3 of Fig. 2.

Referring to the drawings, at 10 is indicated generally a printing or duplicating machine adapted to make the prints by the process hereinbefore described. This includes a printing couple comprising a rotating printing cylinder 11 and a cooperating impression roller 12, together with suitable sheet-feeding equipment 13 and a print receiver 14. Sheet feeder 13 is adapted to forward sensitized print sheets 15 from a feed pile 16 on a suitable feed table 17 singly in succession to the crotch of the printing couple, where they are picked up between the rotating cylinder 11 and the roller 12 and are forwarded through the couple and discharged into the receiver 14. As sheet-handling mechanism of this general nature is well known in the printing and allied arts, specific detailed description thereof is not necessary, it being understood that the cylinder, the feed mechanism and other associated parts of the device are suitably interconnected and may be driven in timed relation from any convenient source of power, not shown.

The cylinder 11 is formed with a support portion 18 adapted to carry the negative, stencil or other master copy to be duplicated, which is translucent to the printing light from a lamp or generator 19, mounted within the cylinder in such a manner that the sensitized sheets are exposed to its light emanations through the master copy during their passage through the printing couple of the machine.

As best shown in Fig. 3, the machine 10 is provided with side frame members 21 between which is disposed the rotatable cylinder 11 and impression roller 12, which roller is journalled at its ends in suitable bearings, not shown. The cylinder 11 may be driven in any convenient way, as by means of a pulley 22 journalled on one of the side frame members 21 and engaged by a driving connection 23 carried by the cylinder, the pulley 22 being in turn actuated by a driving belt 24.

The cylinder 11 comprises a pair of axially spaced head members 26, which may be formed with peripheral flanges 27 and the translucent support member 18, secured to the flanges in any convenient way as by clamp rings 28. The head members 26 are also provided with suitable bearings 29 and 31, by which the cylinder is rotatably mounted in the machine, the bearing 29 rotating on a boss 32 on one of the frame members 21 and the bearing 31 rotating on a removable hollow trunnion 33 on the other frame member.

The support member 18 consists of a cylindrically curved sheet of glass, cellulose acetate, methyl methacrylate or other suitable material which has sufficient mechanical strength and rigidity to space and connect the head members 26 and to support the master copy, and which is sufficiently translucent to transmit the printing light. This support member extends circumferentially of the cylinder a distance at least equal to the length of the print sheets to be used,

terminating in beveled edges 34 and 36, shown in Fig. 2. The edges 34 and 36 are adapted to cooperate with suitable clamp bars 37 so constructed as to conform to and engage the edges to secure the master copy 38 on the surface of the member 18.

The lamp 19 which constitutes the source of the printing light is disposed within the cylinder 11 in position such that the entire surface of the translucent support 18 is exposed to the light at each revolution of the cylinder, being preferably located below and parallel to the cylinder axis. In the form illustrated, the lamp 19 comprises a tubular envelope of quartz, glass or other material suitable for the efficient transmission of the printing light, provided with metal ferrules 39 which close the ends of the tube and which contain electrodes, not shown. The electrodes are connected by conductors 41 to any source of electric current suitable for operation of the lamp. The lamp preferably contains a mixture of argon, or other inert gas, and mercury sufficient to produce in operation a total vapor pressure of about one atmosphere, it being understood that the mercury is vaporized by the electric current upon starting the lamp, and that its vapor forms the conductor for the electric discharge during operation. Lamps of this nature, producing light emanations rich in the range between 3550 A. U. and 3750 A. U., have been designed and constructed, and as the general characteristics of such lamps are well known and understood, more detailed description is not necessary.

The lamp 19 is conveniently mounted in a generally cylindrical housing 42 of sheet metal supporting end members or heads 43 of suitable ceramic material such as fused lava, which is both an electrical insulator and is resistive to heat. These heads are provided with aligned central apertures 44 adapted to receive and support the lamp ferrules 39 and they are removably clamped in the ends of the housing 42 as by means of clamp rings 46. The lower part of the housing 42 may be formed with a longitudinal slot, as shown at 47, for the reception of a lens 48, adapted to collect and concentrate the emanation of the lamp into a relatively narrow beam uniformly disposed across the bottom of the cylinder. This beam, extending across the width of the support member 18, will accordingly sweep the entire translucent surface thereof with the printing light at each revolution of the cylinder, so that the print sheets passing through the printing couple will be uniformly exposed through the master copy 38.

The housing 42, and with it the lamp 19, is adjustably supported in the cylinder from a tubular member 51 removably secured in the cylinder 11 and coaxial therewith. The member 51 is supported at one end by a slip connection 52 with the trunnion member 33, and at the other end by a hollow trunnion or support 53 mounted in the boss 32. The member 51 is axially positioned between the trunnions 31 and 53 and is prevented from turning by means of an interlocking ear and notch connection, indicated at 54. The housing 42 is suspended from the member 51 by adjusting screws 56 and is provided with a take-up spring 57, whereby the housing may be vertically adjusted to focus the beam from the lens 48. The member 51 may be closed near one end by a plug 58, which divides it into shorter and longer portions, and the short portion may be provided with holes 59, by which the conductors 41 are con-

veniently led out through the hollow trunnion 53.

The longer portion of the tubular member 51 constitutes a manifold through which air under pressure may be introduced into the housing 42 to cool the lamp 19. For this purpose the interior of the member 51 is connected, as by a flexible conduit 61, to the interior of the housing 42 near one end thereof, and the outer end of the hollow trunnion 33 is connected as at 62 to any convenient source, not shown, of air under pressure. Such air flowing through trunnion 33, member 51 and conduit 61 into the housing 42 escapes through apertures 63 provided in the head member 43 at the other end of the housing, thereby carrying away some of the heat produced by operation of the lamp 19 and maintaining a proper operating temperature within the housing. To prevent the entrapment of heated air within the cylinder 11 one of the cylinder heads 26 may be provided with escape apertures 64 and the other head with intake apertures 66 which operate to scoop air into the cylinder at one end and discharge it at the other end to assist in controlling the temperature rise.

It will be understood that in operation, the printing cylinder 11 is rotated at a speed adapted to give each print sheet an exposure of the desired duration, as determined by the character of the negative or master copy, the intensity of the printing light and the sensitiveness of the print sheets. As the sheets are fed in succession through the printing couple, each is held in close rolling contact with the negative 38 while the printing light from the lamp 19 is uniformly distributed across the cylinder by the lens 48. In this manner each sheet receives a uniform exposure of the correct length and the finished prints are discharged in succession into the receiver 14.

From the foregoing description it will be evident that my invention provides a simple, clean and entirely dry process for the rapid duplication of copies, which does not require the use of inks, dyes or other color transfer materials, which requires no drying time, which is free of smudging, smearing and offset, and in which the finished prints are immediately available without the necessity of development or further treatment. My process may be freely carried out in daylight or under ordinary artificial light, and requires no dark room or other special precautions against preexposure of the print sheets.

My invention is not based on any theory of the reactions which take place or of the reasons why my light-sensitive materials are irreversibly changed in color by exposure to the particular printing light employed. Not all of the reactions in this complex phenomenon are fully known and it is not desired to limit my invention to any theory of action. It will be understood that various forms of my invention other than those described above may be used without departing from the spirit or scope of the invention.

What I claim and desire to secure by Letters Patent is:

1. The process of preparing sensitizer for use in the photochemical duplication of copies, which comprises first combining hot aqueous solutions of sodium molybdate, of sodium tungstate and of oxalic acid, cooling said hot aqueous mixture to precipitate the sensitizing material, filtering off said sensitizing material and washing said material with alcohol to remove free oxalic acid.

2. A process of duplicating copies comprising sensitizing print sheets with a reaction product of sodium molybdate, sodium tungstate and oxalic acid irreversibly photo-sensitive to light in the spectral band lying approximately between 3550 and 3750 A. U., and exposing said sensitized print sheets through a photo-negative of the copy to be duplicated to light in said spectral band.

3. A process of duplicating copies, comprising sensitizing print sheets with an alkali metal compound of molybdic, tungstic and oxalic acids irreversibly photo-sensitive to light in the spectral band lying approximately between 3550 and 3750 A. U., and exposing said sensitized print sheets through a photo-negative of the copy to be duplicated to light in said spectral band.

4. A process of duplicating copies comprising sensitizing print sheets with a reaction product of alkali metal molybdate, alkali metal tungstate and oxalic acid irreversibly photo-sensitive to light in the spectral band lying approximately between 3550 and 3750 A. U., and exposing said sensitized print sheets through a photo-negative of the copy to be duplicated to light in said spectral band.

5. A print sheet for the duplication of copies which is sensitive to light in the spectral band between 3550 A. U. and 3750 A. U., comprising a base impregnated with the reaction product of a mixture of sodium molybdate, sodium tungstate, and oxalic acid.

6. A print sheet for the duplication of copies which is sensitive to light in the spectral band between 3550 A. U. and 3750 A. U., comprising a base impregnated with the reaction product of a mixture of about one part by weight of sodium molybdate, about one part by weight of sodium tungstate, and about two parts by weight of oxalic acid.

7. A sensitizer for print sheets for the photochemical duplication of copies comprising a reaction product of a mixture of an organic acid, and alkali metal salts of molybdic and tungstic acids.

8. A sensitizer for print sheets for the photochemical duplication of copies comprising a reaction product of a mixture of oxalic acid, and the sodium salts of molybdic and tungstic acids.

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