May 6, 1941. L. P. F. VAN DER GRINTEN 2,241,104

PROCESS AND APPARATUS FOR THE TREATMENT OF PHOTOGRAPHIC COATINGS

Filed April 22, 1939 2 Sheets-Sheet 1

FIG: 1

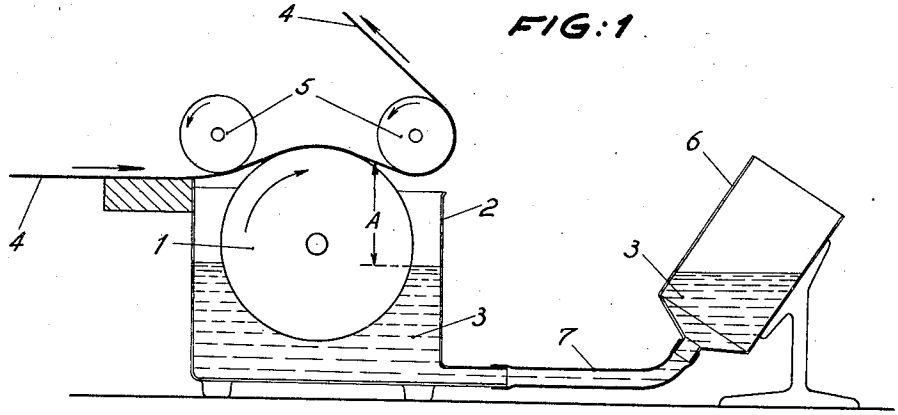


FIG: 2

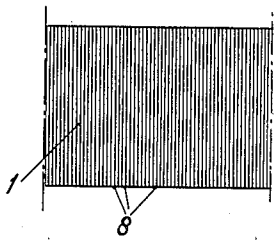


FIG: 3

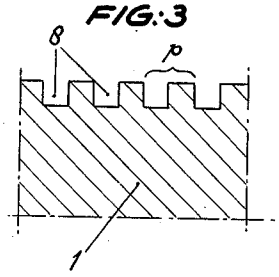


FIG: 4

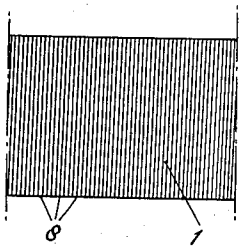


FIG: 5

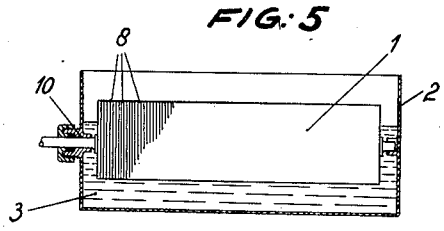


FIG: 8

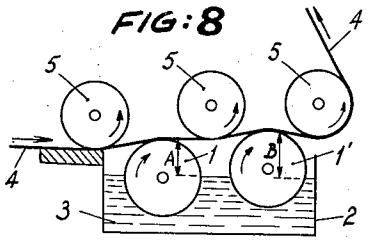


FIG: 6

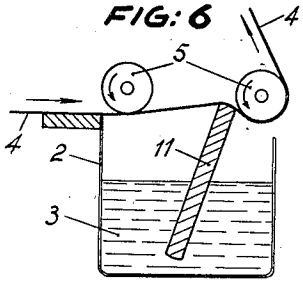
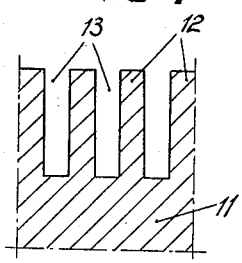


FIG: 7



L. P. F. VAN DER GRINTEN

BY Hammond & Littell

May 6, 1941. L. P. F. VAN DER GRINTEN 2,241,104

PROCESS AND APPARATUS FOR THE TREATMENT OF PHOTOGRAPHIC COATINGS

Filed April 22, 1939 2 Sheets-Sheet 2

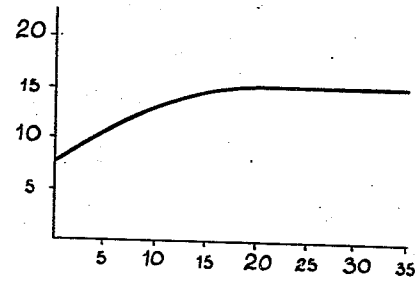


FIG:9

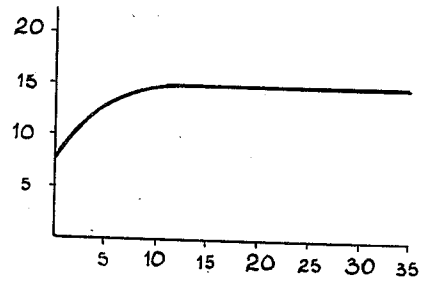


FIG:10

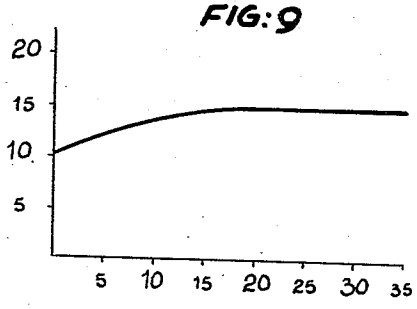


FIG:11

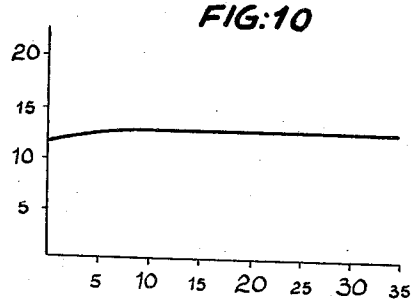


FIG:12

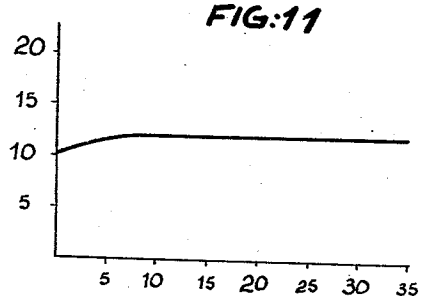


FIG:13

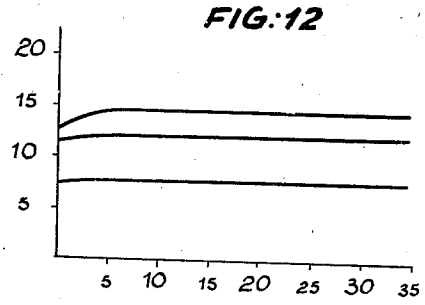


FIG:14

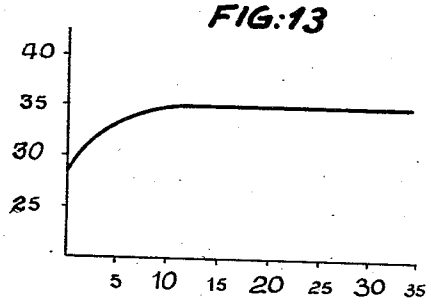


FIG:15

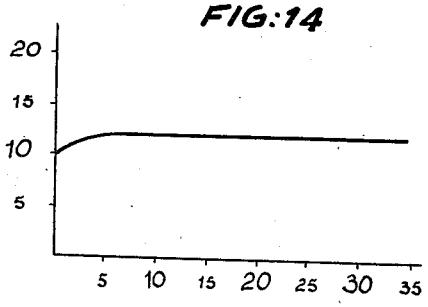


FIG:16

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Hammond & Littell

Patented May 6, 1941 2,241,104

UNITED STATES PATENT OFFICE

2,241,104

PROCESS AND APPARATUS FOR THE TREATMENT OF PHOTOGRAPHIC COATINGS

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Application April 22, 1939, Serial No. 269,430
In the Netherlands January 19, 1939

25 Claims. (Cl. 95—88)

The present invention relates to processes and apparatus for the preparation, development or fixing of photographic coatings or layers on sheets of any length according to the so-called "semi-wet" method.

In the various reproduction processes, especially in making technical reproductions, it is customary to treat material that has been exposed to light, for instance, light-sensitive paper, on one side with a liquid which develops and/or fixes the picture.

While one of the oldest known procedures for the development of silver halide paper is to apply an excess of liquid to the paper with the aid of a roller, (see German Patent No. 198,143), the so-called "thin layer" or "semi-wet" method of development has recently been used to a greater extent. With this "semi-wet" method a definite quantity of liquid is applied, and by this means, depending upon the concentration of chemicals in the solution, a definite amount of chemicals is applied per surface unit of the material to be developed and/or fixed. This method has been described in various publications, including "Chemie en Industrie" (1927), pages 235 and 257, Dutch Patent No. 27,513, British Patent No. 326,568 and British Patent No. 416,489. In general, a roller is used which rotates in a liquid bath, and the material to be developed is passed over this roller. The surface of the roller is generally smooth, but may also be matted (see German Patent No. 664,916). The paper is kept in touch with the roller, for example, by means of a comb (Dutch Patent No. 23,602), by small rotating disks (German Patent No. 561,142 and U. S. Patent No. 1,891,722) or by means of a guide (French Patent No. 692,658). In these, as well as in other processes, the paper runs freely over the roller. Such is not the case, however, with the method of operation described in British Patent No. 295,993, where the paper runs between two rollers which press against each other. In order to handle sheets, means are often employed which lift the wetted sheets off the roller. So in the British Letters Patent 295,993, knives performing the role of cutters run in grooves of the caoutchouc roller, said grooves, of course, closing in the soft caoutchouc and being at a considerable distance one from the other. In the British Letters Patent 326,568 the application roller, for the purpose of arranging cutters, is provided with canals which, however, again are within a considerable distance from each other; these canals are, besides, relatively broad.

It is, furthermore, known that films may be provided with a layer sensitized to light by passing same across a relatively broad canal in which the surface of the liquid is always kept exactly on the upper edge by a communicating connection with a supply vessel having a constant level. This requires that the canal be arranged exactly horizontally.

The "semi-wet" process also is used to apply sensitized coatings. A typical example is the application of a coating of chromate gelatine or chromate gum to metal plates or metallized sheets for the well-known office offset machines. The liquid layer is applied by pouring it onto a horizontal leaf or sheet, which is placed on a whirler so that the excess liquid is flung off and a uniform layer remains. This process, however, is unwieldy, unreliable and uneconomical.

In the use of these known processes, several difficulties are encountered, especially when dealing with sheets of smaller lengths.

In general, not all papers or other materials undergoing treatment need the same quantity of chemicals for proper treatment, and it is impossible, for example, without anything further, to develop a certain diazo type which requires 12 grams per square meter of a certain developer, by applying 6 grams per square meter of a developer in a doubled concentration. The latter may at times penetrate the material insufficiently, or it may crystallize out in the cold in such a concentration.

Conditions are similar when processing other materials according to the "semi-wet" method; for instance, when fixing blue prints. In that case, large quantities of the fixing agent, for instance about 30 grams per square meter, are required according to the present practice in the art. In general, it is desirable to apply the chemicals necessary for the treatment by means of as little liquid as possible per unit area of the material, and in that case, therefore, the amount of liquid depends on the chemicals to be applied. When dealing with different diazo type papers and different chemical materials different quantities of liquid are often desirable, and for that reason it would be of considerable advantage to be able to regulate the amount of the liquid. In the known processes, however, the amount of liquid to be applied to the paper by means of the roller is either incapable of being regulated in practice, or can be regulated only by means that are not always desirable. For instance, larger quantities, above about 20 g. per m.^{2}, can be obtained only by means of strong movement of the roller in a direction opposite to

the paper (strong "counter-run" or "counter-motion"), and smaller quantities, below about 10 g. per m.², only by means of a strong movement of the roller relative to the paper, both in the same direction (strong "advanced run" or "advanced motion") both methods, however, being not entirely harmless. Besides the possibility of applying larger and larger quantities of liquid, the possibility of applying smaller and even very small quantities is at times of great importance.

Furthermore, when using the known methods the amount of liquid applied on the sheet by means of the roller, per square meter of surface area, is not uniform from start to finish. In the beginning, the paper takes along the smallest amount of liquid. This amount increases during the treatment until it reaches a certain value, after which it remains uniform during the further treatment of the particular sheet. For instance, if a sheet din A_4 of a certain paper is developed in the manner described in Dutch Patent No. 27,513, by means of apparatus such as described in Dutch Patent No. 23,602, it is found upon examination that only 6 grams of the fluid are applied per square meter of paper in the beginning and that this quantity increases slowly until it reaches a value of 12 grams per square meter at a distance of approximately 20 cm. from the start of the sheet. This phenomenon is referred to hereinafter as the "starting" and the affected portion of the sheet as the "starter." A distinction is made between the "length" and the "size" of the starter. By the "length" is meant the number of centimeters of the paper which must run over the roller before the maximum amount of liquid is applied. The ratio between the above indicated maximum amount of liquid and the amount of liquid which the paper takes on at the start of the treatment represents the "size" of the starter. In the above-mentioned example, therefore, the length of the starter amounts to 20 cm., and the size to

$$\frac{12}{6}=2$$

The shortest starter, therefore, is naught; the minimum size is unity. A starter is especially annoying on sheets of smaller lengths in view of the fact that no pieces can be discarded therefrom. The application of too little liquid may result in underdevelopment and the application of too much liquid, for instance, in a yellowing of the prints.

It is one of the objects of the present invention to provide a new and improved process for applying "semi-wet" coatings of liquid to sheets of any length in the preparation, development and/or fixing of photographic coatings, which to a large extent overcomes the disadvantages mentioned hereinabove. More specifically, one of the objects of the invention is to provide a new process by which definite amounts of the liquid may be applied per unit area of the sheet.

Another object is to provide such a process in which the application of the liquid may be regulated to suit the requirements of different sheet materials and of different coating liquids.

Another object of the invention is to provide such a process which substantially reduces the difficulties heretofore encountered at the start of each sheet by reducing both the "length" and the "size" of the "starter," thereby producing sheets characterized by improved uniformity and quality of treatment.

A further object of the invention is to provide a process having the qualities just mentioned which at the same time is practical and efficient to operate.

Still another object of the invention is to provide new and improved apparatus for applying "semi-wet" coatings of liquid to sheets of any length in the preparation, development and/or fixing of photographic coatings according to the process herein disclosed.

In accordance with this invention I have found that the foregoing and other valuable objects and advantages may be attained and that in the preparation, development and/or fixing of photographic coatings according to the semi-wet process highly uniform coatings may be formed on sheet material of any length by feeding the material over mechanism for applying the liquid coating and by leading the liquid in a multiplicity of minute canals to the place where the material leaves the applying mechanism. The multiplicity of minute canals are located so close together that a substantially uniform layer or coating is applied over the entire width of the sheet. The sheet is preferably passed freely over the mechanism.

The sheets to be treated according to this invention may be made of the most varied types of material. Paper, of course, is one of the most typical materials. Besides paper, however, other sheet materials may be so treated, such as metallized paper, metal foil, cellulose compounds and the like.

The invention may be used in practice in various physical embodiments. For example, in one embodiment of the invention the minute canals may be provided by minute tubes, which may be placed in one or more rows and disposed with their lower ends extending into the liquid; the material to be treated is then passed over the upper ends of the tubes.

In another embodiment the canals may be provided by minute grooves. These grooves are not necessarily provided with "bottoms." For example, a liquid applying device in a form simulating a comb, in which the spaces between the "teeth" provide the minute canals, gives advantageous results.

In another embodiment of the invention, the coating is applied to the sheet material in a multiplicity of minute streams by leading the liquid to the material in a multiplicity of canals in or on the surface of a roller, which may be either stationary or rotary. The canals are conveniently provided by grooves in the roller. They may also be provided by wires or the like which have been wound or otherwise arranged around the roller. If the "roller" is of the stationary type it need, of course, not be a rotary body.

One of the important features of the present process, in which the device for applying the coating may be either stationary or rotary, is that the amount of liquid applied per unit area of the paper may be regulated readily within the limits encountered in practice. When using the invention for treating ordinary papers, for example, it is possible to apply less than 5 grams of liquid, and over 35 grams, per square meter of paper, and this without need for a heavy advanced run or counter run. In case of pronounced roughness of the sheet and of greater viscosity of the liquid, such as when preparing chromate coatings on rough metal surfaces, still larger quantities, such as 50 grams per square meter and more, are obtainable. This regula-

tion is effected quite simply, namely, by regulating the distance between the surface of the liquid and the place where the sheet leaves the application device. This distance is referred to below as the "level distance." If the level distance is decreased, other constants remaining the same, a larger quantity of the liquid is applied, and vice versa.

The level distance may be regulated very easily if it is dependent on the height of the liquid in a liquid bath; in such a case, the liquid bath is connected with a liquid container which is located relatively higher or lower. The applying device consequently reaches more or less into the liquid. If a roller having a large diameter is used as the applying device, it may be necessary to allow the roller to run in stuffing box glands, or to have the roller pins, the motion device and other parts extending into the liquid.

Another important feature of the new process is that it substantially improves the starter. For instance, a starter may be obtained which has a length of only a few centimeters and a size approaching unity. Of course, it is not possible to obtain such ideal starters in all examples of operations, but a great improvement over the known practices may be ascertained in almost all examples, especially over practices involving the use of known roller devices at normal speeds. Of course, there is no improvement with respect to the starter in comparison with the practice of whirling chromate plates, but that process possesses other disadvantages, as mentioned above, with which the present process is not afflicted.

In this invention it is of special advantage that in the case of a rotary roller it is unnecessary to resort to a varied speed and/or direction of roller and paper in order to bring about the above described advantages: the desired effects may be achieved by running the roller and the paper in the same direction with the same speed ("parallel run" or "parallel motion"). This advantage is of especial significance when friction between the roller and the sheet is to be avoided, for instance, because of the appearance of ruptures, and when, in the case of a smooth roller, it would be necessary to work either with a considerable advanced run or with a counter run in order to obtain at least somewhat satisfactory results. This, of course, does not preclude the fact that in special cases friction between the paper and the applying device may give specific advantages, for instance, a counter run for the application of very large amounts of liquid.

The special requirements which the minute canals as used according to this invention must meet in certain cases depend on the nature of each particular case. For example, should the canals be too wide, the fluid may not be applied in a sufficient amount. In this respect, the question whether capillary action must be relied on entirely for the provision of the liquid (as in the case of stationary applying devices), or whether other means must provide therefore (such as friction in the case of rotary coating devices), or both, also should be considered. If the canals are too far apart irregularities occur, while under certain circumstances the process is no longer effective.

Further objects and advantages of the invention and details of preferred manners of practicing the same will appear from the following more detailed description, when considered in connection with the accompanying drawings, in which:

Fig. 1 represents a cross section of an apparatus for applying a semi-wet coating on a sheet according to the invention.

Fig. 2 represents a side elevation of a part of the roller 1 of Fig. 1.

Fig. 3 represents a longitudinal section along a profile line of a part of the roller 1 of Fig. 1 on an enlarged scale.

Fig. 4 represents a side elevation of an applying device having helical grooves.

Fig. 5 represents a cross section of a roller the journals of which are immersed in the coating liquid.

Figs. 6 and 7 represent an applying device similar to a "comb," Fig. 6 being a cross section and Fig. 7 a side elevation of a part thereof on an enlarged scale.

Fig. 8 represents a cross section of an apparatus provided with two applying rollers.

Figs. 9–16 represent graphical indications of various types of "starters."

In Fig. 1 the applying device in the form of a roller 1 is mounted in a trough 2 containing the fluid 3 to be applied. The sheet 4 is guided by guide rollers 5, the rollers 1 and 5 and the sheet 4 running in the directions of the arrows. A vessel 6 mounted for vertical adjustment has a flexible communicating connection 7 with the trough 2 in order to enable the operator to increase or to decrease the level distance A.

In Fig. 2 the parallel lines 8 represent the small grooves or canals in the roller 1 of Fig. 1, by which grooves or canals the fluid from trough 2 is applied to the sheet 4 (see Fig. 1). These grooves or canals are shown in Fig. 3 at a larger scale, p representing the period of the canals.

Instead of crossing the axis of the roller vertically the canals 8 may form a helical curve with reference to the axis of the roller, as represented in Fig. 4.

In Fig. 5 the roller 1 has its journals 10 immersed in the liquid 3 in the trough 2.

In Fig. 6 the trough is again represented by the figure 2. It contains the fluid 3 to be applied on the sheet 4, said sheet being guided by rollers 5 over the applying device 11. As follows from Fig. 7 this device is similar to a comb, parts 12 forming the "teeth" and the spaces 13 between the teeth forming the minute canals, without "bottoms."

In Fig. 8 the sheet 4 is guided by three guide rollers 5 over the applying rollers 1 and 1'. Both rollers 1 and 1' are provided with minute canals as described in connection with Figs. 2 and 3; the level distance B of roller 1' is larger than that (A) of roller 1.

The starter in Fig. 9 corresponds to the one which may be obtained from a process which is now mostly used, having smooth rollers and "parallel motion" (same speed of sheet and roller in the same direction). Fig. 9 therefore represents the status of the technique as to the process with parallel motion. In Fig. 10 the starter is shorter while being of like size, the one in Fig. 11 is smaller while being of like length, and it may, for instance, in mechanisms with "counter motion" (roller runs in opposite direction to paper) be obtained in accordance with the prevailing technique.

Fig. 12 represents a typical starter obtained by using the new process, said starter having a length of only a few centimeters and a size of 1.05.

The other graphs will be elucidated as the specification proceeds.

In a typical and simple example of performance of this invention, one uses a roller surface with a profile reproduced in Fig. 3. The canals 8 run around the whole of roller 1. Calculated on one of the profile lines the canals have a definite total cross section per dm. of the length of the roller. In Fig. 3 this cross section is equal to the width of the canals multiplied by their depth and again multiplied by their number per dm. length. This entire cross section per dm. length of the application device is inidcated below by the word "passage." Experiments show that already with rollers of a small passage, for instance, of about 2 mm.^{2}, a considerable capability of regulating the amounts of liquid to be applied has been achieved, which even surpasses the result of a matt surfaced roller. A great improvement in the starter when applying amounts of liquid of about 10 g. per m.^{2} is achieved with a passage of about 20 to 30 mm.^{2}.

Conditions are similar in other examples of performance with respect to the use of stationary as well as rotary application devices.

One may obtain a certain passage by means of a larger number of small canals or by means of a smaller number of large canals. In the former case, the distance of the canals, the "period" p is small, in the latter case large. Within certain limits, the effect in accordance with this invention is more or less independent of this variation. For practical considerations, construction of device, accessibility for cleaning the canals, and the like, one will, of course, not choose any exceedingly small canals and periods, while the effect in accordance with this invention will, of course, be lessened with periods beyond a certain size, whereby the liquid layer is applied in stripes of more and of less liquid. This fact has already been pointed out. When using rollers with canals placed vertically to the axis this condition becomes evident, for instance, even when using a period of approximately 5 mm.; and when still larger periods are used, for instance of 15 mm., it may prevent operation.

One may also obtain a certain passage by providing for narrow deep or broad shallow canals. Also in this respect, practical limits are set to the breadth and depth: to the depth, for instance, by the strength of the application device, to the breadth because too broad canals, same as too large periods, may cause disturbances, such as the occurrence of stripes, and the like. Breadths of more than 0.5 mm., may already cause damage when applying fluids with a viscosity of about that of water. The data given here are, however, not absolute data as the appearance of these disturbances is to a certain degree dependent on the level distance, i. e. to the effect that a lessening of this distance counteracts the appearance of stripes or tracks. Also an increase of viscosity of the liquid has, for instance, an effect in this respect. Besides, these disturbances are more of a hindrance for one kind of work than for another.

Also the speeds of the sheet and of the roller, if any, have a certain influence. In general, a greater speed of the sheet or leaf shows an effect similar to a smaller level distance. This holds true with regard to advanced runs, parallel runs, backward runs (movement of the roller in the same direction as the sheet but at a smaller speed), standstills and counter runs, of which each, however, again has a specific effect on the amount of the fluid, i. e. somewhat to the effect that the advanced run applies less and the counter run more.

From the foregoing it must be deduced that the canals may show a different form of the cross section. I have already mentioned round and rectangular cross sections, they may also be in the shape of a V, which form is named here because same is easily obtainable in practice. Canals with a V shaped cross section in general produce the effect desired in accordance with this invention, but sometimes in a lesser degree than the rectangular canals.

As a rule, one may say that the canals need not follow the line of the shortest distance between the level of the liquid and the place where the sheet leaves the application device. This means, for instance, with respect to rollers, that the canals need not cross the axis of the roller vertically; they may, for instance, also be arranged in the nature of a helical curve in or on the surface of the roller, as represented in Fig. 4. One may also use canals cutting across each other. As a borderline-case, one may in the case of rotary application devices construct the canals in the longitudinal direction of these devices.

In general, one may also state that the starter is better when applying small amounts of liquids than larger ones.

As a matter of fact the greatness of the effect obtained in accordance with this invention depends on still other factors than those described, for instance, on the composition of the liquid used, and the moisture content of the paper; this applies especially to the amount of fluid applied per m.^{2}. At any rate, however, the improved effect in comparison with the use of a smooth or matt surfaced roller is evident when other constants remain the same.

Compared to the process working with matt-surfaced rollers or with devices having felt or brush surfaces, the process provided by this invention has also the advantage that the devices are less subject to being worn out and becoming dirty and they may be cleaned easily, which fact applies especially to devices with open, easily accessible canals.

This invention is, of course, not limited to a process where the application device, for instance, a roller, is partly in the fluid, although this method of operation at the moment may be considered as the most practical one; one may, of course, also supply fluid to the application device in other ways, for instance, with auxiliary rollers. The conception of "level distance" is then, of course, to be revised. This invention is also not limited to working with only one application device; one may also work, for instance, with two or more rollers; also when supplying liquid several times to the sheet or also when applying it once or several times on both sides of the sheet, this invention may be used to advantage.

This process is of special importance when applied to the so-called semi-wet method of preparing and developing, or to the semi-wet fixing of diazotypes and blue prints and, for instance, when preparing chromate gelatine or chromate gum layers on leaves, sheets and the like, for the technique of printing, for instance, when preparing offsets. In all of these processes it is important to obtain, from the beginning, an exact and variable adjustment of the amounts of liquid over the entire surface, according to the particular process being used.

Also, if layers, especially diazo layers, should

be contained in cellulose surfaces or should be applied therein, a good treatment is possible in accordance with this invention which treatment very often meets with difficulties when the usual smooth or matt surfaced rollers, i. e. rollers not provided with canals, are used, especially when running parallel. It is surprising that it is possible to work in accordance with these processes, without meeting with difficulties, by means of application devices provided with canals, and that thereby one may obtain such technically important advantages.

The forwarding of the sheets may be accomplished with rollers; before the application of the layer of liquid, for instance, with rollers which touch the sheet on both sides; shortly after application by means of a roller touching only the untreated side; after the absorption of the liquid into the sheet, again with two rollers, as before the application. If one applies small quantities, for instance 5 g. per m.^{2}, one may let the forwarding device touch the treated side also almost directly upon application. One may also let the roller applying the liquid take the paper along itself or the roller may be taken along by the moving paper. Furthermore, upon the application of the liquid, a device may be so installed as to wipe off the so-called stained edge which may be sometimes found on the edge of the sheet, as well as a blotting roller, while the drying may also take place upon application of the liquid by means of a coupled drying device.

A stained edge especially occurs when the applying device is a rotating roller and may be objectionable as soon as more than about 7 g. liquid per m.^{2} must be applied to the sheet. If, however, two or more applying devices are provided in such a manner that the last one [which is one of a type provided by this invention] when working alone would—for the rest under the same conditions—apply less liquid on the sheet than the device adjusted before the last one when working alone in its turn, the stained edge is much decreased and separate means for removing said edge may be dispensed with. For reasons of an easy transport of the end of the sheet a parallel-motion roller is preferably used as the final applying device. This method is of special importance when developing diazo type copies.

In principle, when applying the process according to the preceding paragraph, the applying device or devices adjusted before the final one need not necessarily be of the type according to the present invention; they may rotate or stand still; when using rollers as these devices, said rollers may be smooth or matted. It is preferred, however, not only to provide the final applying device with minute canals in accordance with the present invention but also the other ones. Preferably the last mentioned ones have also the form of rollers and, when in use, rotate in the same direction and with the same speed as the sheet travels (parallel motion).

There are several manners in which the apparatus can be built or operated to the effect that the last applying device will apply less liquid on the sheet than the preceding one in the sense which has already been described. For example, this may be achieved by using a roller as an applying device preceding the final one and operating said roller with a sufficient countermotion; if said preceding roller is one according to the present invention an additional advantage is obtained; only a small starter is caused by said roller.

Another, very simple manner consists in regulating the quantity of liquid applied by the final applying device in relation to that applied by the preceding one with the aid of the level distance of the final device. If both final and preceding device are formed in accordance with the present invention it is possible, of course, also to regulate the quantity of liquid supplied by the preceding device by means of its level distance; if in this case two similar rollers are used this amounts to arranging the preceding roller so that it works with a smaller level distance than the final one (Fig. 8: the level distances are A and B).

If in the last mentioned embodiment the difference in level distance amounts to more than 10 mm., spots may be found on the sheet. A difference in level distance between 3 and 7 mm., for example a difference of 5 mm., has proved to yield good results.

If the measures described above for decreasing the stained edge are chosen well, two applying devices, for example two rollers, are nearly always sufficient. This is of practical importance as this is simpler than the use of more applying devices.

The application devices of the present invention may be prepared from any material suitable therefor, for instance, from suitable metals which may, if desired, be provided with corrosion-resistant surfaces, such as chromium, and the like. Also, stainless steel is especially suitable; furthermore glass, synthetic resins, hard rubber, and the like may be used. In most instances, when a roller is used, same is driven mechanically. In case of appliances without a motor, one draws the paper across the roller and this then turns the roller. The starter is then generally less beautiful, but one still gets the advantages of the present invention.

The following examples may illustrate the invention. For simplicity's sake, one has always worked with an applier placed in a trough containing a fluid, which permits the level distance to be expressed more exactly in figures. For convenience's sake, one takes here as the level distance the vertical distance between fluid level and the line which has been drawn parallel to this level through the place where the sheet leaves the applier (Fig. 1, distance A).

Example I

A sheet made of the usual suitable raw material paper of 110 g. per m.^{2} with a pH of approximately 4, which was prepared in the usual manner with approximately 15 cm.^{3} per m.^{2} of a solution of

	Per cent
p.Diazo-ethyl benzyl aniline chloride	2
Thio urea	3
Oxalic acid	1
Gelatine	0.2

and then dried to a moisture content of approximately 3%, is exposed under a transparent original and thereupon developed with a solution of

	Per cent
Phloroglucinol	0.6
Resorcinol	0.6
Thio urea	2
Thio sulfate	6
Soda	3
Borax salt	1
Sodium salt of isopropyl naphthalene sulfonic acid	0.1

In the process of developing, the sheet runs over a mechanism as reproduced diagrammatically in the cross section of Fig. 1. Roller 1 and sheet 4 run both in the direction of the arrows with a speed of 2 m. per minute. The roller has a diameter of 35 mm. and is provided with small canals in accordance with Fig. 3. The small canals have a width of 0.4 mm., a depth of 0.6 mm. and a period p (Fig. 3) of 0.8 mm., so that the passage amounts to 30 mm.² per dm. length. The level distance A is 10 mm. In this manner, the developer is distributed over the sheet as shown in Fig. 13, whereby a good black development of the diazo type copy is obtained with about 12 g. per m.². The starter is about 1.2 and has only a length of approximately 9 cm.

If one adds to the developing fluid 1½% of glycol mono butyl ether, one may obtain a similar development with a still smaller and shorter starter and a little larger fluid quantity per m.²; or with the same fluid quantity at a somewhat lesser speed or a somewhat greater level distance.

Example II

One works as described in Example I with the developer without glycol mono butyl ether, but with small canals having a breadth of 0.25, a depth of 1.2 and a period of 0.6 mm., i. e. with a passage of 50 mm.² per dm. length. One then obtains the results stated in the table below which have been reproduced in curves in Fig. 14.

Level distance	Speed of sheet and roller (parallel run)	Starter	Quantity of liquid per m²	Curve in Fig. 15
Mm.			*Grams*	
10	4 m. per sec.	Size ±1.1, length ±5 cm.	±14	*a*
15	5 m. per sec.			
10	2.7 m. per sec.	Size ±1.05, length ±3 cm.	±12	*b*
15	4.1 m. per sec.			
15	1.4 m. per sec.	Size 1.0, Length: nil.	±7½	*c*
25	4 m. per sec.			

If one works in accordance with *a*, one may, for instance, dilute the developer with about 15% water which may be desirable in cold weather. If one works in accordance with *c*, one may take about 4% of soda in lieu of 3% and one then obtains a quicker drying print of a somewhat browner color.

Example III

One makes the preparation as mentioned in Example I with a solution of:

	Per cent
Para-diazo diethyl aniline chlorstannate	2.6
Tartaric acid	4
Boric acid	3
Thio urea	3
Phloro glucinol	0.3

and develops in a solution of

	Per cent
Soda	10
Sodium thio sulfate	8
Sodium salt of iso propyl naphthalene sulfonic acid	0.1

As described in Example I, for this development the sheet runs over a rotary roller. The sheet has a speed of 2 m. per minute and the developing roller has a speed of 0.8 m. per minute (backward run). The roller has a diameter of 35 mm. and small canals, as shown in Fig. 3. The small canals have a breadth of 0.25 mm., a depth of 1 mm. and a period of 0.6 mm. and consequently a passage of about 40 mm.² per dm. length. The level distance is 28 mm.

In this way, one obtains a good development with about 5½ g. of the developer per m.², obtaining a very good starter.

Example IV

One makes the preparation as shown in Example III but one develops with ammonia liquid having a specific weight of 0.90. The development is made as follows:

Roller and sheet are both running with a speed of 2.3 m. per minute in the same direction (parallel run). The roller has a diameter of 25 mm. and is provided with canals as shown in Fig. 3. These have a breadth of 0.25 mm., a depth of 0.8 mm. and a period of 1.2 mm. so that the passage is ±16 mm.² per dm. length. The level distance is 20 mm. One obtains a beautifully black developed print, while the quantity applied amounts to 7 g. per m.² The starter is practically not much bigger than the one shown in Fig. 14.

One may carry through this development in a closed vessel in order to avoid the annoyance of ammonia vapors, in which the developed print may also be de-aerated. Since the quantity of fluid applied is only small, one may touch both sides of the print shortly after application and therefore forward it with rollers or other means.

Example V

One makes the preparation as described in Example I, but with a solution of:

	Per cent
Diazo-1-benzoyl amino-4-diethoxy-2-5-benzol chlorostannate	2.5
Citric acid	2
Boric acid	1

and develops with a solution of:

	Per cent
Soda	2
Phloroglucinol	1
Borax	0.5
Sodium salt of iso propyl naphthalene sulfonic acid	0.1

For the purpose of developing, the sheets run over a roller in accordance with Example III. Sheet and roller have both a speed of 1 m. per minute in the same direction. The level distance is 25 mm. The quantity applied for the developing is only 4½ g. per m.² The diazo type copy is of a beautiful violet-brown color. The starter is practically nil.

If one works in the same manner, but with a developer, consisting of:

	Per cent
Sodium acetate	10
Phloroglucinol	1
Sodium salt of isopropyl naphthalene sulfonic acid	0.1

one obtains the same results, but the diazotype copy has a darker violet-brown tone than the former. It therefore develops that, working in accordance with this invention, one may apply very small liquid quantities with an excellent result without the necessity of resorting to a considerable first run and the disadvantages coupled therewith.

Example VI

One makes the preparation as in Example I, but with a solution of:

	Per cent
Ferric ammonium oxalate	8
Potassium ferric cyanide	4
Secondary sodium phosphate	2
Gelatine	0.2

and fixes with a solution of:

	Per cent
Primary ammonium phosphate	10
Phosphoric acid spec. weight 1.3	3
Zinc sulfate	10
Ammonium persulfate	6
Sodium salt of the sulfuric acid ester of the oleic acid butyl ester	0.1

For this fixation, the sheet runs in an apparatus in accordance with Fig. 1 over a roller which, however, rotates in opposite direction to the sheet. The sheet has a speed of 2 m. per minute, the roller one of 3½ m. per minute (in opposite direction). The roller is the same as described in Example III. The level distance amounts to 10 mm. The distribution of the fixing agent over one sheet is shown in Fig. 15. The quantity amounts to about 35 g. per m.² with a starter of about 1.25 (35:28) and length of about 10 cm. One obtains a negative blue print in light cream-yellow line on a dark blue background which shows in practice a sufficiently great stability to light.

Example VII

One prepares row material paper of the kind as indicated in Example I but with a somewhat rougher surface, i. e. in the customary manner per m.² with about 15 cm.³ of a solution of:

	Per cent
Para-diazo ethyl benzyl aniline chloride	1.3
Thio urea	3
Oxalic acid	1
Gelatine	0.2

whereupon the paper is dried to a moisture content of about 3%. The prepared surface is provided with a fine powderlike mixture consisting of equal parts of water-free soda and phloroglucinol. Then one develops in an apparatus in accordance with Fig. 1 with ordinary water by applying thereof about 5 g. per m.². One uses as a roller the one shown in Example III. The level distance amounts to 25 mm. Paper and roller run both with a speed of 1½ m. per minute.

One obtains black, sharp, positive pictures which dry directly.

Example VIII

Paper is prepared and developed with the fluids disclosed in Example I. When developing, the sheet runs over a stationary metal device 11, which reaches down into the developing fluid 3, as shown in Fig. 6. As appears from the longitudinal cross section shown in Fig. 7 the device has the shape of a comb; its thickness is 2 mm. With a period of 2 mm. canals 13 are provided having a breadth of 0.25 mm. and a depth of 15 mm. The level distance amounts to 10 mm. and the paper has a speed of 4 m. per minute.

The result of this development is as shown in Fig. 16. The starter is about 1.2 and has only a length of about 5 cm.

By regulating the level distance and the speed of the paper, one may regulate the quantity of fluid applied in a similar manner as in Example II.

Example IX

A matt-surfaced aluminum sheet, pasted on paper, as is used for offset machines in offices, is passed with a speed of 2 m. per minute over a roller having a diameter of 35 mm. which roller is provided with small canals in accordance with Fig. 3. The small canals have a period of 0.6 mm., a breadth of 0.4 mm. and a depth of 0.5 mm., so that the passage amounts to a little over 30 mm² per dm. length.

The roller rotates in a small trough containing a fluid of:

	Parts by weight
Potassium bichromate	6
and	
Gummi arabicum	23
in	
Distilled water	100

The temperature of the solution amounts to about 20 degrees C. The level distance is 8 mm.

At a speed of the roller of 1.5 m. per minute (therefore with a small backward run) about 45 g. of fluid per m.² is applied; at a roller speed of 2 m. per minute (in the same direction) about 50 g. are applied. If one gives the roller a speed of 2.5 per minute (i. e. small advanced run) one applies about 55 g. fluid per m.². (In this case, the somewhat greater viscosity of the fluid causes apparently a small deviation from the rule that less is applied when applying advanced run.)

After drying, the aluminum sheet is ready for further preparation for the offset type of the office machines.

The starter obtained in this manner is without importance. If one works under the same conditions with a smooth roller one does not obtain a uniform preparation of the aluminum sheet.

One may also work with other rollers, for instance, with a roller having small canals with a period of 0.6 mm., a width of 0.25 mm. and a depth of 0.6 mm.; therefore with a passage of 25 mm.² per dm. length. Due to such a small cross section of the canals there is, however, a little tendency, in parallel runs at any rate, to form small air bubbles on the prepared surface.

With a roller having V-formed canals of 37 degrees and a width of 0.4 with a period of 0.4, in other words with canals lying next to each other, one obtains good results even in parallel runs.

In connection with the viscosity of the fluid it is to be stated that these results, of course, cannot be obtained at any low temperature whatsoever.

Example X

An acetyl cellulose film of approximately 65 g. per m.² is saponified on one side and prepared on the saponified side with a solution of 5% paradiazo ethyl benzyl aniline chloride and 2% tartaric acid. Upon drying, a copy is prepared on this film either by transmitted light or by the usual reflectography or in the manner of the screen reflectography, whereupon the film is pasted on paper by means of casein in diluted latex. For this purpose, the side of the film to be pasted on is provided with a thin layer of this latex solution and the paper likewise. After both layers are dry, they stick together by themselves when pressed well.

The film pasted on in this manner is now developed with the developer in accordance with Example I in an apparatus having a roller as used in Example III. The lever distance is 12 mm. and the sheet and the roller both run with a speed of 2 m. per minute (parallel run). [It is also possible to use a small backward run (roller speed 1.5 m. per minute) or a small advanced run (roller speed 2.5 m. per minute)].

Without any hindering starter, a 12 g. per m² developer is applied which gives a beautifully black copy. No usable result was obtained with the aid of a smooth roller with other constants remaining the same.

Instead of taking a film of 65 g. per m² and pasting same, one may take a film of 100 g. per m.² which is not necessary to paste.

Example XI

One works as in Example I using, however, the apparatus which has been shown in Fig. 3. The rollers 1 and 1' and sheet 4 are all running with a speed of 2.3 m. per minute in the direction indicated by the arrows. Rollers 1 and 1' have a diameter of 25 mm. and are both provided with rectangular canals (Fig. 3) having a breadth of 0.3 mm., a depth of 1.2 mm. and a period of 1.0 mm. so that the passage amounts to 36 mm.² per dm. length of the roller. The level distance A is 12.5 mm., the level distance B is 17.5 mm. In this way 11 g. of liquid per m.² of the sheet are applied; the starter is very small and short and the sheet leaves roller 4' almost without stained edge.

If both rollers had worked with the same level distance, for example of 15 mm., then the stained edge would have been greater and it would have been recommendable to take measures for removing same, for example by wiping, blotting, additional drying and so on.

Furthermore an operation along the lines of this example gives less rise to an unequal supply of liquid on the sheet on account of unevennesses in the sheet than does a process in which only one roller is used.

Of course it is also possible to have rollers 1 and 1' running in separate troughs.

What I claim is:

1. A method of developing or fixing light-sensitive sheets of any length according to the so-called semi-wet process which comprises leading a developing or fixing liquid from a supply thereof to a zone of application in a multiplicity of closely-spaced minute streams and passing the sheet over said zone in contact with said liquid in said zone, said streams being spaced apart such a small distance that a substantially uniform quantity of the liquid is applied over the width of the sheet.

2. A method according to claim 1, characterized in that the sheet is pressed freely over said zone.

3. A method of developing or fixing light-sensitive sheets of any length according to the so-called semi-wet process which comprises leading a developing or fixing liquid from a supply thereof to a zone of application in a multiplicity of closely-spaced minute streams of rectangular cross-section and passing the sheet over said zone in contact with said liquid in said zone, said streams being spaced apart such a small distance that a substantially uniform quantity of the liquid is applied over the width of the sheet.

4. A method of developing or fixing light-sensitive sheets of any length according to the so-called semi-wet process which comprises leading a developing or fixing liquid from a supply thereof to a zone of application in a multiplicty of closely-spaced minute streams of a V cross-section and passing the sheet over said zone in contact with said liquid in said zone, said streams being spaced apart such a small distance that a substantially uniform quantity of the liquid is applied over the width of the sheet.

5. A method of developing or fixing light-sensitive sheets of any length according to the so-called semi-wet process which comprises leading a developing or fixing liquid from a supply thereof in a multiplicity of closely-spaced minute streams to an elongated zone of application extending transverse to said streams and passing the sheet over said zone in contact with said liquid in said zone, said streams having a total cross section of at least 2 mm.² per dm. of length of said zone and being spaced apart such a small distance that a substantially uniform quantity of the liquid is applied over the width of the sheet.

6. A method of developing or fixing light-sensitive sheets of any length according to the so-called semi-wet process which comprises leading a developing or fixing liquid from a supply thereof to a zone of application in a multiplicity of closely-spaced minute streams and passing the sheet over said zone in contact with said liquid in said zone, said streams being spaced apart with a period of less than 15 mm. such that a substantially uniform quantity of the liquid is applied over the width of the sheet.

7. A method of developing or fixing light-sensitive sheets of any length according to the so-called semi-wet process which comprises leading a developing or fixing liquid from a supply thereof to a zone of application in a multiplicity of closely-spaced minute streams and passing the sheet over said zone in contact with said liquid in said zone, said stream being spaced apart with a period of less than 5 mm. such that a substantially uniform quantity of the liquid is applied over the width of the sheet.

8. A method according to claim 1 in which the minute streams of liquid are united into a thin band of liquid extending transverse to the direction of movement of the sheet at said zone of application.

9. A method of developing or fixing light-sensitive sheets according to the so-called semi-wet process which comprises leading minute streams of a developing or fixing liquid from a supply thereof by a multiplicity of closely spaced minute canals on the periphery of a roller to a zone of application on said roller, passing the sheet over said zone in contact with said liquid in said zone, and simultaneously rotating said roller, said streams beng spaced apart such a small distance that a substantially uniform quantity of the liquid is applied over the width of the sheet.

10. A method of developing or fixing light-sensitive sheets according to the so-called semi-wet process which comprises leading minute streams of a developing or fixing liquid from a supply thereof by a multiplicity of closely spaced minute canals on the periphery of a roller to a zone of application on said roller, passing the sheet over said zone in contact with said liquid in said zone, and simultaneously rotating said roller in the direction of movement of said sheet and at a corresponding peripheral speed, said streams being spaced apart such a small distance that a substantially uniform quantity of the liquid is applied over the width of the sheet.

11. A method of developing or fixing light-sensitive sheets of any length according to the so-called semi-wet process which comprises leading a developing or fixing liquid from a supply thereof to a zone of application in a multiplicity of closely-spaced minute streams, passing the sheets over said zone in contact with said liquid in said zone, and regulating the amount of liquid applied to the sheets by varying the distance between said zone and the level of the liquid supply, said streams being spaced apart such a small distance that a substantially uniform quantity of the liquid is applied over the width of the sheets.

12. In an apparatus for developing or fixing

light-sensitive sheets according to the so-called semi-wet process, means adapted to be held in contact with a supply of developing or fixing liquid for applying a layer thereof onto the sheets, said means having the shape of a comb the teeth of which form closely-spaced minute channels therebetween, said channels extending between the liquid supply and a zone of application spaced therefrom and being spaced apart a distance sufficiently small to apply a substantially uniform layer of the liquid over the width of sheets passed across said zone.

13. Apparatus for developing or fixing light-sensitive sheets of any length according to the so-called semi-wet process comprising container for holding a supply of developing or fixing liquid and means in contact with the supply liquid for applying a layer thereof onto the sheets, said applying means comprising at least two rollers arranged in spaced relation with their axes horizontal and each having a multiplicity of closely-spaced minute channels on its periphery forming a connection between the supply liquid and a zone of application spaced therefrom, the channels of each roller being spaced apart a distance sufficiently small to apply a substantially uniform layer of the liquid over the width of sheets passed across the corresponding zone of application, said zone of the final roller being at a greater distance from the supply liquid than said zone of the preceding roller.

14. Apparatus for developing or fixing light-sensitive sheets of any length according to the so-called semi-wet process comprising a rigid member for applying developing or fixing liquid to the sheets and means for supplying such liquid to said member, said member formed with capillary means for leading such liquid in a multiplicity of mintue streams from the liquid supply to a zone of application spaced therefrom, said capillary means comprising a multiplicity of closely-spaced minute canals of such small width and so closely spaced as to apply a substantially uniform layer of the liquid over the width of sheets passed in contact with liquid in said zone.

15. Apparatus for developing or fixing light-sensitive sheets of any length according to the so-called semi-wet process comprising a rigid member for applying developing or fixing liquid to the sheets and means for supplying such liquid to said member, said member formed with capillary means for leading such liquid in a multiplicity of minute streams from the liquid supply to a zone of application spaced therefrom, said capillary means comprising a multiplicity of separate, closely-spaced, parallel, minute canals having open sides in a common plane extending from such supply to said zone and of such small width and so closely spaced as to apply a substantially uniform layer of the liquid over the width of sheets passed in contact with liquid in said zone.

16. In an apparatus for developing or fixing light-sensitive sheets of any length according to the so-called semi-wet process, means for applying developing or fixing liquid to the sheets comprising a roller adapted to be contacted by a supply of the liquid and having on its periphery capillary means for leading the liquid in minute streams from such supply to a zone of application spaced therefrom, said capillary means comprising a multiplicity of minute parallel canals open at the periphery of the roller and of such small width and so closely spaced as to apply a substantially uniform layer of the liquid to sheets passed in contact with liquid in said zone.

17. In an apparatus for developing or fixing light-sensitive sheets of any length according to the so-called semi-wet process, means for applying developing or fixing liquid to the sheets comprising a roller adapted to be contacted by a supply of the liquid and having at its periphery capillary means for leading the liquid in minute streams from such supply to a zone of application spaced therefrom, said capillary means comprising a multiplicity of minute parallel canals open at the periphery of the roller and of such small width and so closely spaced as to apply a substantially uniform layer of the liquid to sheets passed in contact with liquid in said zone, said canals extending vertically with respect to the axis of said roller.

18. In an apparatus for developing or fixing light-sensitive sheets of any length according to the so-called semi-wet process, means for applying developing or fixing liquid to the sheets comprising a roller adapted to be contacted by a supply of the liquid and having at its periphery capillary means for leading the liquid in minute streams from such supply to a zone of application spaced therefrom, said capillary means comprising a multiplicity of minute parallel canals open at the periphery of the roller and of such small width and so closely spaced as to apply a substantially uniform layer of the liquid to sheets passed in contact with liquid in said zone, said canals defining a helical curve with respect to the axis of said roller.

19. Apparatus for developing or fixing light-sensitive sheets of any length according to the so-called semi-wet process comprising a rigid member for applying developing or fixing liquid to the sheets, having a multiplicity of separate, closely-spaced, minute canals adapted to form a connection between a supply of such liquid and an elongated zone of application spaced therefrom and operative to lead the liquid by capillary action to said zone in a multiplicity of minute streams, said canals having a total cross-sectional area of at least 2 mm.^{2} per 100 mm. of length of said zone, having a period of less than 5 mm. and being so closely spaced as to apply a substantially uniform layer of the liquid to sheets passed across said zone in contact with liquid therein.

20. Apparatus for developing or fixing light-sensitive sheets of any length according to the so-called semi-wet process comprising a rigid member for applying developing or fixing liquid to the sheets, formed with a multiplicity of separate, closely-spaced minute canals adapted to extend between a supply of such liquid and an elongated zone of application spaced therefrom and operative to lead the liquid by capillary action to said zone in a multiplicity of minute streams, said canals being of rectangular cross-section and being so closely spaced as to apply a substantially uniform thin layer of the liquid to sheets passed across said zone in contact with liquid therein.

21. Apparatus for developing or fixing light-sensitive sheets of any length according to the so-called semi-wet process comprising a rigid member for applying a developing or fixing liquid to the sheets, formed with a multiplicity of separate, closely-spaced minute canals adapted to extend between a supply of such liquid and an elongated zone of application spaced therefrom and operative to lead the liquid by capil-

lary action to said zone in a multiplicity of minute streams, said canals being of V-shaped cross-section and being so closely spaced as to apply a substantially uniform thin layer of the liquid to sheets passed across said zone in contact with liquid therein.

22. Apparatus for developing or fixing light-sensitive sheets of any length according to the so-called semi-wet process comprising a rigid member for leading developing or fixing liquid from a supply thereof and for applying the liquid directly to the sheets, said rigid member formed with a multiplicity of separate, closely-spaced minute canals adapted to extend between such supply and a zone of application spaced therefrom and operative to lead such liquid by capillary action to said zone in a multiplicity of minute streams, said canals each having a width not exceeding about .4 mm., said canals being so closely spaced as to apply a substantially uniform thin film of the liquid to sheets passed over said zone in contact with liquid therein.

23. Apparatus for developing or fixing light-sensitive sheets of any length according to the so-called semi-wet process comprising a rigid member for leading developing or fixing liquid from a supply thereof and for applying the liquid in a uniform thin film directly to the sheets, said rigid member formed with a multiplicity of closely-spaced minute canals adapted to extend between such supply and an elongated zone of application spaced therefrom and operative to lead such liquid to such zone in a multiplicity of minute streams, said canals having a period not exceeding 1.2 mm.

24. Apparatus for developing or fixing light-sensitive sheets of any length according to the so-called semi-wet process comprising a rigid member for leading developing or fixing liquid from a supply thereof and for applying the liquid in a uniform thin film directly to sheets passed thereover in an elongated zone of application spaced from such supply, a face of said member adapted to extend between such supply and such zone having formed therein a multiplicity of closely-spaced minute canals open at said face and operative to lead liquid to said zone in a multiplicity of minute streams, each of said canals having a width not exceeding .4 mm. and said canals having a total cross-sectional area not exceeding about 50 mm.^{2} per 100 mm. of length of said zone.

25. Apparatus for developing or fixing light-sensitive sheets of any length according to the so-called semi-wet process comprising a container for holding a supply of developing or fixing liquid, a roller mounted for rotation about a horizontal axis in contact with liquid in said container and sheet feeding means for passing sheets freely across said roller at a zone of its periphery spaced above the level of contact with liquid in said container, the periphery of said roller formed with capillary means for leading liquid in a multiplicity of minute streams from such supply to said zone, said capillary means comprising a multiplicity of minute, parallel canals extending transverse to the axis of said roller and open in a common plane at the periphery thereof, said canals being of such small width and so closely spaced as to apply a substantially uniform layer of liquid to sheets passed across said zone in contact with liquid therein.

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