Dec. 13, 1955 H. L. J. WASTEELS 2,726,588

APPARATUS FOR THE PRODUCTION OF PHOTOGRAPHIC IMAGES ON VARIOUS MATERIALS

Filed March 26, 1951 2 Sheets-Sheet 1

Fig. 1

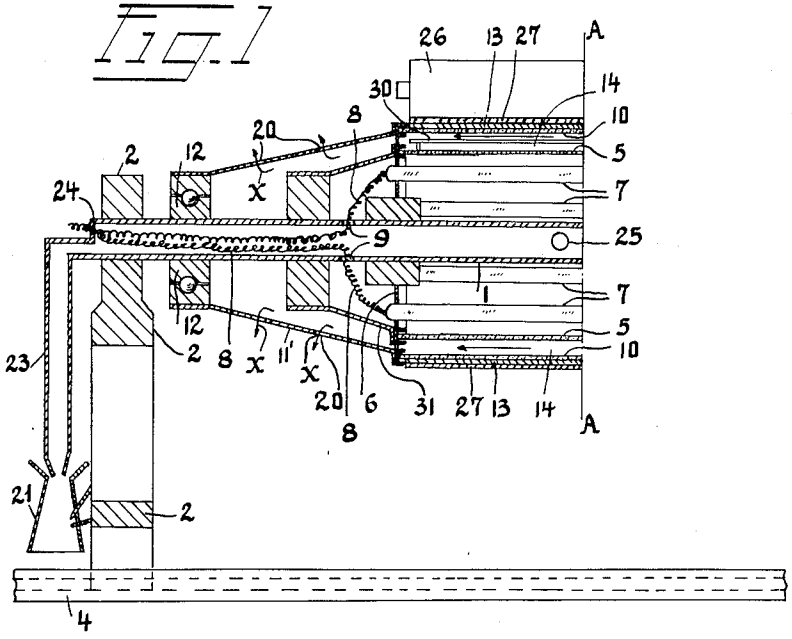

Fig. 2

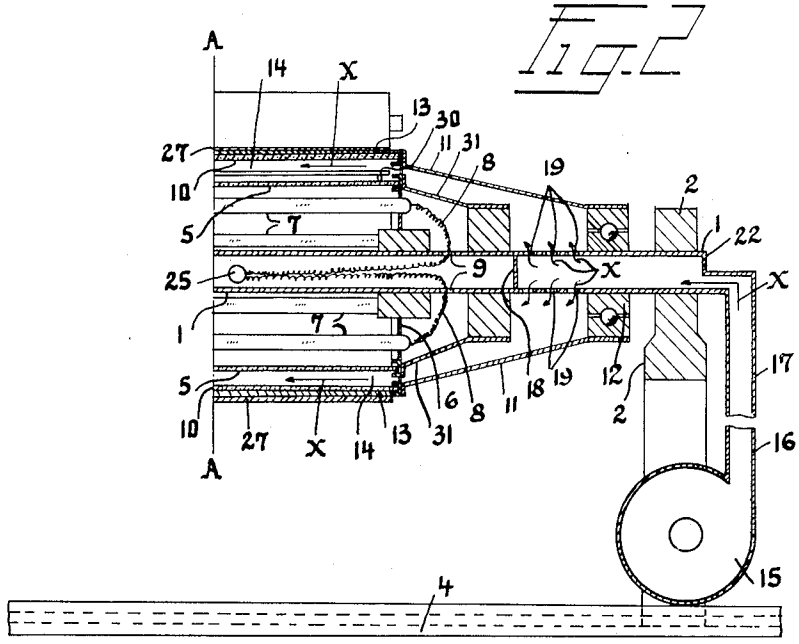

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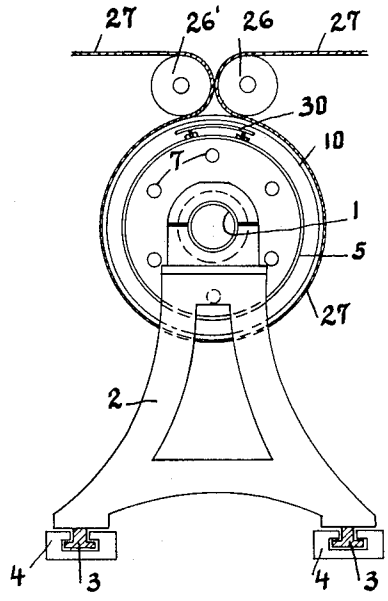
Fig. 3



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APPARATUS FOR THE PRODUCTION OF PHOTOGRAPHIC IMAGES ON VARIOUS MATERIALS

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Claims priority, application Belgium March 28, 1950

4 Claims. (Cl. 95—77.5)

The present invention relates to an apparatus for the production of photographic images on various materials.

The invention is concerned especially with the continuous production of photographic images by a process and with the aid of an apparatus by means of which the images are formed at high speed.

By the expression "various materials" there must be understood, in the present specification, a large variety of materials including actual textile materials having a base consisting of natural fibres of animal, vegetable or mineral origin, or a base of synthetic fibres in the form of fabrics, felts, texoids (fibres agglomerated with the aid of a binder), papers, etc., if desired provided with a protective coating or the like, as well as materials assimilable or analogous to textile materials, such as the flexible sheets obtained by casting, rolling or stratification, etc., notably sheets of natural or synthetic rubber, sheets having a base consisting of synthetic resins, such as polyvinyl resins, superpolyamides, etc., as also solid materials, such as pasteboard, wood, metals, plastic materials, ceramic materials, glasses, agglomerates having a base consisting of fibres, wood, etc.

In the usual processes for the printing of textile materials, it is the current practice to deposit on a textile material a solution, emulsion, suspension or paste containing a colouring agent or a substance capable of forming a colouring agent, and/or a mordant or a corrosive.

The design or pattern of the impression is obtained, in these usual processes, by localising the deposition of the printing solution, emulsions, suspension or paste on certain parts of the textile or like material, by employing for discontinuous operation marking sheets, pads, stencil sheets or so-called "lyonnais" or silk-screen frames, and, for continuous printing, engraved rollers or cylinders, for example of bronze.

The development and fixing of the various colouring agents take place in various ways, depending upon the nature of the colouring agents, notably by vaporisation, passage between rolls, etc.

It is known that shades having good resistance to light and to washing may be obtained by the formation of azo colouring agents on the textile fibres. These processes, which constitute dyeing processes, consist for example in subjecting the fabrics to a grounding with the aid of coupling agents, such as naphthols, and in thereafter forming the desired colouring agent by development in a bath containing a diazo compound. In these processes, a simple coupling takes place, no photo-chemical or photographic process being employed. These dyeing processes have the disadvantage of being costly because the consumption of colouring compounds is high.

In addition to the known printing and dyeing processes hereinbefore defined, processes for the production of photographic images on textile materials are also known. In these processes, in which use is made of silver or iron salts, diazo sulphonates, bichromated colloids, etc., photographic images are formed by means of luminous energy, that is to say, the fabric is coated with compounds capable of forming colouring agents, the formation and/or appearance of these colouring agents being conditioned by the application of light, notably of actinic light, a screen or image carrier being preferably disposed between the course of light and the material to be treated.

These processes for the printing of textile materials by the formation of photographic images have a number of disadvantages, including the high cost of the ingredients, especially in cases where silver salts are employed, the number and complexity of the operations, the low resistance of the images obtained to water and light, the relatively small output of the photo-sensitive compounds, such as diazo sulphonates, the high degree of humidity required by the material in order to be sufficiently sensitive to light, the overflowing of light-sensitive material on the negatives, which is sometimes such that the negatives become covered with a fog or are soiled and are thus rapidly rendered unserviceable, and the rapid formation of a colouring agent on the surface of the material treated, this colouring agent forming a screen and preventing the penetration of light into the fibres of the material when the latter consists of a fabric, the colouring agent formed only on the surface having low resistance to chemical and physical actions.

The present invention has for its object to provide a process for the production of photographic images, not only on textile materials or similar flexible materials, but also on solid materials, notably wood, metals, plastic materials, etc., the process according to the invention having none of the disadvantages of the usual processes and being very simple.

According to the invention, there is applied over the entire area of the material to be treated at least one diazo compound, the said material is subjected to the action of an actinic light, so as to destroy the diazo compound in predetermined zones of the surface of the material, and the diazo compound remaining on the material, that is to say the diazo compound which has not been destroyed by the actinic light, is subjected to the action of at least one coupling agent.

The invention differs from the combined use of diazo sulphonates and coupling agents in that it is characterised by the photochemical destruction of materials capable of subsequently forming a colouring agent under a suitable treatment, and not by the photochemical formation of a colouring agent, by reason of the fact that actual diazo compounds are employed and not substances capable of forming diazo compounds. In the process according to the invention, as applied to a textile material, the light destroying the photosensitive material penetrates into and through the fibres. The images are consequently obtained on the two faces of this textile material. The semi-dyes are constituted of colouring agents which are formed, not superficially, but actually within the fibres.

By reason of the process of photochemical destruction, the absence of coupling agents at the instant when the actinic light acts and the reduction of the degree of humidity, the image carriers are not impaired, while the printing speed is considerably increased.

The application of the diazo compound over the entire material to be treated may be effected, in the process according to the invention, in the manner known per se by aerograph spraying by passage between rollers, by coating by means of a doctor or by means of a gumming machine. After the application of the diazo compound, the material in question is preferably dried before being subjected to the action of a source of actinic light, which may consist of one or more mercury vapour tubes, developing for example a power of from 3000 to 3500 watts.

Finally, the material which has undergone the action of the actinic light so that in certain predetermined zones of

its surface the diazo compound has undergone a deterioration such that it is no longer capable of coupling, is treated by a coupling agent, for example by vaporisation or passage between rollers, which produces a colouring agent depending upon the nature of the diazo compound and of the coupling agent at the points at which the diazo compound in question has not undergone the action of the actinic radiations.

In accordance with one feature of the invention, there is disposed between the material which has undergone locally the destructive action of the actinic light and the source of actinic light, a screen having parts pervious to the latter light and parts impervious thereto, according to the pattern or image which it is desired to obtain on the material in question.

The screen in question may consist of an image formed on a suitable support. By way of example of screens suitable for carrying the invention into effect, there may be cited photographic pellicles, films or plates which may be hardened and which bear either a negative or a positive image, ruled screens, stencil plates, designs on any transparent or translucent supports, designs on tracing paper, tracing cloths, diazotypes, etc.

In accordance with a further feature of the invention, the material is subjected to a continuous movement with respect to the source of actinic light, while the aforesaid screen is preferably simultaneously actuated with a movement in the same direction and at the same speed as that of the aforesaid material.

When it is desired to obtain photographic images continuously on a web of textile material or similar flexible material, the latter and the aforesaid screen are subjected to a rotational movement about the source of actinic light, the screen preferably being in contact with the textile or like material, while the latter is subjected to the action of the actinic radiations. In this case, the screen preferably consists of an endless photographic film.

The diazo compounds with the aid of which the material is sensitised over its entire area include, according to the invention, compounds belonging to the class containing diazo and tetrazo bases, the salts of diazonium and tetrazonium, the double salts of metal and diazonium derivative, the internal anhydrides of diazo compounds, etc. Particular examples of such diazo compounds are the chloride of N-phenyl-4-aminobenzene diazonium, the chlorozincate of N:N-diethyl-4-aminobenzene diazonium, the sulphate of N-phenyl-4-aminobenzene diazonium, the internal anhydride of 2-diazo-1-naphthol-5-sulphonic acid, and the diazo derivatives of 5-amino-benzoylamino-1:4-diethoxybenzene, of p-amino-hydroxyethylaniline, of p-amino-dimethylaniline, of p-amino-mono-ethyl-o-toluidine, etc., excluding diazosulphonates and hydrazine-sulphonates.

Coupling agents which give rise to the development of a colouring agent by reaction with a diazo compound include coupling agents containing no water-solubilising groups, such as napthols and the derivatives thereof, notably those commercially known as Naphthols AS and constituted generally by arylides of aryloxy-carboxylic acids or by ketones. As particular examples of such coupling agents there may be cited o-toluidide of 2:3-hydroxyanthracene carboxylic acid, diacetylacetolidide, 5-chloro-2-toluidide of 2:3-hydroxynaphthoic acid, the o-toluidide of 2:3-hydroxy-naphthoic acid, 1-hydroxy-naphthyl-4-ähenyl acetone, etc.

The process according to the invention makes it possible to produce images having excellent resistance to washing and to light. The images obtained in accordance with the invention may obviously be subjected to known treatments, notably to treatments, for example with metallic salts or formaldehyde, having the effect of modifying the shade of the colouring agents produced on the fibres, of fixing the shade of these colouring agents, of improving their resistance to chemical agents and to physical treatments, etc.

The process according to the invention, as applied to textile materials or the like, is in addition compatible with the usual dyeing processes. Thus, the textile materials or the like may be dyed before or after the formation of photographic images by the process according to the invention.

In the following are given a number of examples of methods of operation for carrying out the process according to the invention.

Example I

An acetate rayon fabric is "sensitised" by passage between rollers with the aid of an aqueous solution containing 10 grammes per litre of N-phenyl-4-amino-benzene diazonium chloride. After drying, the fabric is exposed to actinic radiations behind an image carrier or screen, some zones of which are pervious to the said radiations, while other zones are impervious thereto.

The fabric is then passed into a bath consisting of a solution containing per litre: 15 grammes of Naphthol AS–GR or 5 grammes of ortho-toluidide of 2:3-hydroxy-anthracene carboxylic acid, 45 cc. of ethanol, and 6 cc. of caustic soda solution at a concentration of 38° Baumé.

After development in the latter bath, the fabric is rinsed with hot water, moderately heated in the presence of a soap solution, rinsed again in hot water and dried. The image obtained is green.

Example II

A viscose rayon fabric is vaporised with the aid of an aqueous solution containing 10 grammes per litre of N:N-diethyl-4-aminobenzene diazonium chlorozincate. After local exposure to light, the fabric is impregnated with the aid of an aqueous solution containing per litre: 10 grammes of phenylmethylpyrazolone and 10 grammes of caustic soda solution (38° Baumé).

The fabric is subsequently treated in the manner indicated in Example I, whereby a red image is obtained.

Example III

A viscose rayon fabric is coated with a paste or an aqueous solution of N-phenyl-4-aminobenzene diazonium chloride. The fabric is dried and subjected at predetermined points to the action of actinic radiations and "developed" in an aqueous bath containing per litre: 15 grammes of p-anisidide of 2:3-hydroxynaphthoic acid, 30 cc. of 50% ammonium sulphoricinate, and 6 cc. of caustic soda solution of a concentration of 38° Baumé.

When rinsed and dried, the fabric bears an image of violet shade.

Example IV

A cotton fabric is "sensitised" as in Example II. After predetermined zones of the fabric have been subjected to the action of a source of actinic light, the fabric in question is "developed" by atomisation with the aid of an aqueous solution containing per litre: 10 grammes of beta-naphthol and 6 cc. of caustic soda solution (38° Baumé).

After rinsing and drying, an image of brownish-violet tint is obtained.

Example V

A sheet of white wood is vaporised with the aid of a solution of N-phenyl-4-amino-benzene diazonium chloride. After drying, the sheet in question is exposed to the action of actinic radiations through an image carrier or screen bearing, for example, an image representing the grain of a precious wood, such as mahogany, Brazilian rosewood, etc.

The sheet of white wood is then subjected to the action of a developing agent, such as phenylmethylpyrazolone.

It is thus possible to fix on sheets of ordinary wood, images which, as the applicant has observed, bear an extraordinary resemblance to those of the grain of a precious wood.

The applicant has also conducted experiments on other materials, such as metals, pasteboard, paper, texoids, plastic materials, etc., in which methods of operation corresponding substantially to those of Examples I to V were employed.

It is obvious that the process according to the invention is not exclusively limited to the methods of operation described in the foregoing examples and that many modifications may be made to these methods of operation, both with regard to the nature of the chemical compounds employed, and with regard to the proportions and conditions in which the latter are employed, without departing from the scope of the present invention.

The present invention also concerns an arrangement for continuously producing photographic images on textile materials or similar flexible materials by the process described and defined in the foregoing.

The arrangement according to the invention comprises essentially a fixed hollow shaft mounted on supports, a first cylinder consisting of a material pervious to actinic light, rigidly mounted on the aforesaid shaft concentrically in relation thereto, at least one source of actinic light mounted in the first cylinder and a second cylinder consisting of material pervious to actinic light, concentric to the first cylinder and of larger diameter than the first cylinder, the second cylinder being mounted on the aforesaid fixed shaft and arranged to turn about the first cylinder.

According to one feature of the arrangement according to the invention, the first cylinder comprises two flat end members or cheeks perpendicular to the aforesaid fixed shaft and having formed therein orifices affording passage to tubes for the generation of actinic light, while the second cylinder comprises two conical end members or cheeks mounted on the aforesaid fixed shaft through bearings, at least one of the conical end members of the second cylinder being detachable.

According to another feature of the invention, the arrangement comprises means for maintaining a circulation of air or of a cooling fluid between the aforesaid cylinders, while it preferably comprises in addition means for setting up a pressure reduction within the first aforesaid cylinder.

Other details and features of the arrangement according to the invention will become apparent in the course of the following description of the accompanying drawings, which show diagrammatically merely by way of example, one embodiment thereof, and in which:

Figures 1 and 2 each show in vertical longitudinal section a part of the arrangement, Figure 1 showing the part to the left of the dot-and-dash line A—A, and Figure 2 showing the other part to the right of the line A—A, and Figure 3 is an end view of the arrangement.

In these two figures, the same reference numerals designate identical elements.

The arrangement illustrated in the drawings comprises a hollow shaft **1** rigidly mounted on two supports **2** arranged to slide at their lower ends **3** in longitudinal rails **4** so as to enable the arrangement to be moved in a direction parallel to the axis of the hollow shaft **1**.

The hollow shaft **1** supports a first cylinder **5** consisting of a material pervious to actinic radiations, for example quartz or silicate glass, and rigidly mounted on the said hollow shaft **1**. Formed in the flat end plates or cheeks **6** of the cylinder **5** are apertures through which there extend tubes **7** for the generation of actinic light. The conductor wires **8** connected to the ends of the tubes **7** penetrate into the hollow shaft **1** through orifices **9** therein, outside the first cylinder **5**. As will be seen from Figure 1, the hollow shaft **1** thus serves as a sleeve for the passage of the said conductor wires **8**.

A second cylinder **10**, also consisting of a material pervious to actinic radiations, is mounted concentrically to the first cylinder **5**. The second cylinder **10** is of larger diameter than the first cylinder **5** and is supported by two

conical members or cheeks **11** and **11'** arranged to turn on the hollow shaft **1** with the aid of a ball, needle or roller bearing **12**. The second cylinder **10** serves as a support for a photographic image carrier **13** bearing the image which it is desired to reproduce on the textile or like material to be treated. Instead of serving as a support for a photographic image carrier **13**, the second cylinder **10** may itself be converted into an image carrier by engraving or by any other suitable method.

The conical end members or cheeks **11** and **11'** are preferably detachably mounted on the hollow shaft **1** so as to permit the removal of the second cylinder **10** with the photographic carrier supported thereby and the replacement of the latter cylinder by another bearing a different photographic carrier.

In the annular space **14** between the cylinders **5** and **10** there is preferably maintained a circulation of air or other cooling fluid. The means employed for effecting this circulation comprise a blower **15**, the discharge duct **16** of which communicates with a duct **17** leading to one end **22** of the hollow shaft **1**. Provided in this shaft **1** is a partition **18**, in front of which the shaft **1** has orifices **19** through which the cooling air may penetrate into the conical end member or cheek **11** of the second cylinder **10**. This air follows the path indicated by the arrows X. After having passed into the annular gap **14** between the cylinders **5** and **10**, the air is collected in the conical end member **11'** of the second cylinder, whence it escapes through orifices **20** formed in the side wall of the conical end member **11'**.

The circulation of air or other cooling fluid through the gap **14** has the object of sufficiently cooling the second cylinder **10** to prevent the actinic radiations from damaging the photographic image carrier, and the textile or like material passing around the said cylinder **10**.

In order to increase the cooling action afforded by the circulation of air, means are provided to set up within the first cylinder **5** a pressure reduction which inhibits the transmission of the heat developed by the tubes **7**. The means for setting up the pressure reduction in question comprise a vacuum pump **21** which communicates through a duct **23** with the end **24** of the hollow shaft **1**, the communication between the interior of this hollow shaft and the interior of the first cylinder **5** being afforded by the orifices **25** formed in the said shaft **1**.

Two guide rollers **26** and **26'** arranged close together are provided in the upper part of the second cylinder **10**. The function of these guide rollers will be explained later.

In order to prevent the actinic radiations from acting on the textile or like material before the latter is secured against the periphery of the cylinder **10** or against the photographic image carrier **13** supported thereby, a screen **26** is provided in the annular gap **14** between the cylinders **5** and **10** and is supported by the first cylinder **5**.

Finally, in order to ensure a fluid-tight separation between the first cylinder **5** and the second cylinder **10**, there are provided within the end members or cheeks **11** and **11'** of the second cylinder two conical elements **26** which constitute to some extent a second end member for the cylinder **5**. These conical elements **26** are keyed on the hollow shaft **1** in the same manner as the flat cheeks **6**.

The operation of the arrangement described in the foregoing will now be briefly described. A web of textile or like material **27**, which has been coated by aerograph spraying, by passage between rollers or the like, with the aid of a diazo compound sensitive to actinic radiations, and dried, is fed on to the guide roller **26**, which applies the said web **27** against the photographic image carrier **13** supported by the second cylinder **10**. The web of textile or like material is subjected, while situated on the periphery of the cylinder **10**, to the action of the actinic radiations generated by the tubes **7**. As has already been stated, the photographic image carrier **13** allows the actinic radiations to pass at certain points, and these

radiations destroy the diazo compound applied to the corresponding parts of the web 27.

At the instant when it leaves the cylinder 10, the web 27 is taken up by the second roller 26', whence it is driven towards the installation at which the coupling is effected with the aid of a coupling agent at those points of the web at which the actinic radiations have been unable to destroy the diazo compound owing to those parts of the image carrier 13 which are impervious to these radiations.

During the rotation of the cylinder 10, a circulation of air or other cooling fluid is maintained in the annular space 14 between the cylinders 5 and 10 by the operation of the blower 15, while a vacuum is created within the cylinder 5 by operation of the vacuum pump 21.

It is obvious that the details of the embodiment of the arrangement according to the invention as described in the foregoing are only illustrative and that numerous modifications may be made in the form, the arrangement and the constitution of some of the elements employed in the construction of this arrangement, provided that these modifications are not contradictory to the subject of the following claims.

I claim:

1. An apparatus for continuously obtaining photographic images upon textile materials or similar flexible materials comprising a hollow fixed shaft, means for supporting said shaft, a first fixed cylinder of a material permeable to actinic light mounted fixedly and concentrically upon said shaft, a source of actinic light mounted in said first cylinder, a second cylinder also of a material permeable to actinic light, concentric to said first cylinder and having a diameter greater than that of said first cylinder, said second cylinder being rotatively mounted on said fixed shaft, an endless photographic image carrier carried by said second cylinder, a passage between the interior of said hollow shaft and the interior of said first cylinder and means for creating through said hollow shaft and said passage a vacuum at the interior of said first cylinder.

2. An apparatus for continuously obtaining photographic images upon textile materials or similar flexible materials comprising a hollow fixed shaft, means for supporting said shaft, a first fixed cylinder of a material permeable to actinic light mounted fixedly and concentrically upon said shaft, a source of actinic light mounted in said first cylinder, a second cylinder also of a material permeable to actinic light, concentric to said first cylinder and having a diameter greater than that of said first cylinder, said second cylinder being rotatively mounted on said fixed shaft, an endless photographic image carrier carried by said second cylinder, a passage between the interior of said hollow shaft and the interior of said first cylinder and means connected to an end of said hollow shaft to create in said first cylinder a vacuum through said shaft and the passage established between said shaft and the interior of said cylinder.

3. An apparatus for continuously obtaining photographic images upon textile materials or similar flexible materials comprising a hollow fixed shaft, means for supporting said shaft, a first fixed cylinder of a material permeable to actinic light mounted fixedly and concentrically upon said shaft, a source of actinic light mounted in said first cylinder, a second cylinder also of a material permeable to actinic light, concentric to said first cylinder and having a diameter greater than that of said first cylinder, said second cylinder being rotatively mounted on said fixed shaft, an endless photographic image carrier carried by said second cylinder, a passage between the interior of said hollow shaft and the interior of said first cylinder, means for creating a vacuum in said first cylinder through said hollow shaft and the passage established between said shaft and the interior of said first cylinder and means for circulating a cooling fluid in the annular space between said first cylinder and said second cylinder.

4. An apparatus for continuously obtaining photographic images upon textile materials or similar flexible materials comprising a hollow fixed shaft, means for supporting said shaft, a first fixed cylinder of a material permeable to actinic light mounted fixedly and concentrically upon said shaft, a source of actinic light mounted in said first cylinder, a second cylinder also of a material permeable to actinic light, concentric to said first cylinder and having a diameter greater than that of said first cylinder, said second cylinder being rotatively mounted on said fixed shaft, an endless photographic image carrier carried by said second cylinder, a passage between the interior of said hollow shaft and the interior of said first cylinder, means connected to an end of said hollow shaft for creating in said first cylinder a vacuum through said shaft and the passage established between the interior of said shaft and the interior of said first cylinder, a partition in said shaft, a second passage between the interior of said shaft and the annular space provided between said first cylinder and said second cylinder, said second passage being established between said partition and the other end of said shaft, and means connected to the other end of said hollow shaft circulating a cooling fluid in the annular space between said first cylinder and said second cylinder.

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