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POST PROCESSING CURL CONTROL FOR PHOTOGRAPHIC PRINTS

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1

This invention relates to methods for treating paper to reduce or eliminate curl, particularly for treating photographic paper upon which a photographic emulsion has been coated.

Paper which has been coated with gelatin or a similar composition especially for photographic purposes may tend to curl upon drying, rendering the prints difficult to mount and to handle. Efforts to straighten these curled prints may result in a damaged surface, creased paper and cracked images. Consequently, in the past, various means have been suggested for removing or reducing the curl of photographic prints. Mechanical rollers or flexers used alone may result in myriad small cracks in the coated surface. Steaming the support side of the print and flexing the print while in a steamed condition to reduce the effect of the mechanical treatment is disclosed in U. S. Patent 1,880,451. This method, however, requires a steam supply and is not suitable for the use of a small scale photofinisher or by the amateur photographer who wishes to eliminate print curl.

In addition, various "print flattening" solutions have been used which contain chemical compositions such as ethylene glycol, glycerol, diethylene glycol, and the like. These compounds depend upon their hygroscopic nature to accomplish whatever benefit is obtained by their use. Furthermore they must have an atmosphere of relatively high humidity to be effective.

The above methods of post processing curl control are generally unsatisfactory when the photographic paper is handled at low relative humidity, for instance in hot air driers, because the hygroscopic, gelatin plasticizing agents such as glycerol and the like must be able to absorb moisture from the air. Moreover, they are completely ineffective in retarding shrink of the gelatin emulsion layer. These chemical agents are also of little value in reducing the brittleness of the gelatin emulsion at low relative humidity. Furthermore, there is some evidence that the hygroscopic type gelatin plasticizers commonly used (i. e. glycerol, diethylene glycol and the like) actually promote shrinkage and brittleness of gelatin and similar materials at low humidity conditions.

One object of this invention is to provide a method of treating photographic prints so that they can be made to lie flat without manual operations. Another object of our invention is to provide a method of flattening prints which does not in any way injure the prints and which will render them permanently flat. A further object

2

of this invention is to provide a "print flattening" solution which can be used easily to reduce and eliminate post processing curl from photographic prints at low relative humidity conditions. Another object of this invention is to provide a "print flattening" solution which will not cause gelatin shrinkage and will not reduce the mechanical strength of the paper.

The objects of this invention are achieved by treating the photographic prints with certain long chain, non-hygroscopic organic chemicals which plasticize gelatin and reduce post process curl. The use of these chemicals after washing the photographic prints but before drying, not only reduces the magnitude of the curl, but also permits all curl to be removed with a "print straightener" even at low relative humidity without cracking the gelatin emulsion layer. The preferred method of applying these long-chain plasticizers is by soaking the photographic prints to thoroughly impregnate the gelatin layer. However, it is also within the scope of our invention to apply the "print flattening" solution to the gelatin surface.

We have discovered unexpectedly that long-chain ethers may be used to achieve the objects of this invention. Among these long-chain ethers, we have discovered that ethers with recurring ethoxy groups are particularly effective. Examples of ethers of this type are tetraethylene glycol dimethyl ether

$$CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2OCH_3$$

and diethylene glycol diethyl ether

$$CH_3CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_3$$

However, it will be observed from the description herein that certain other ethers of this type may be used and are within the scope of this invention.

As an illustration of this invention, samples of photographic paper were processed through a normal cycle. However, before drying, samples were soaked in a water solution of the plasticizing agent, then were dried in the normal manner. After drying the samples were conditioned in 50% relative humidity and then were moved to 18% relative humidity. When equilibrium in 18% R. H. was reached, curl measurements were made, and while still in 18% R. H., the prints were put through a Morse "print straightener." Emulsion cracking that resulted from this mechanical flexing was rated by marking off small rectangular areas on the prints, and counting the number of cracks per linear inch

within the rectangles. Following are examples of curl and cracking data obtained using non-hygroscopic plasticizers:

Example I.—High speed projection type, photographic paper, single weight

Plasticizer	Conc. in Water, percent	Soak Time, min.	Curl,[1] percent	Cracks per Inch
Tetraethylene glycol dimethyl ether	10	30	−6.3	0
Diethylene glycol diethyl ether	10	30	10.0	1
Non-treated comparison			30.0	9

Example II.—High speed projection type, photographic paper, single weight

Plasticizer	Conc. in Water, percent	Soak Time, min.	Curl,[1] percent	Cracks per Inch
Tetraethylene glycol dimethyl ether	10	15	16	1
Do	15	15	14	1 (avg.)
Do	20	15	15	1 (avg.)
Non-treated comparison			39	4

Example III.—Medium speed contact type, photographic paper, single weight

Plasticizer	Conc. in Water, percent	Soak Time, min.	Curl,[1] percent	Cracks per Inch
Tetraethylene glycol dimethyl ether	15	15	−10	0
Non-treated comparison			34	7

[1] Curl ratings were obtained by measuring the chord of the semi circle the 8 x 10 print forms as it curls, subtracting this value from the dimension when the sheet is flat, and expressing the remainder as percentage of the dimension when the sheet is flat. Positive curl ratings are for curl toward the emulsion side (axis across the print, per cent of the 10 inch length), and negative curl ratings are where too much control was applied and the paper curled away from the emulsion side (axis shifts 90° to length direction, and ratings are per cent of 8 inch width).

The above examples show that long chain plasticizers which are non-hygroscopic, will reduce post processing curl and permit greater mechanical flexing without cracking the gelatin emulsion layer than print flattening solutions previously used. Our work indicates that a concentration of approximately 15% plasticizer in water is ideal, and that the amount of curl control can be regulated by the soaking time. However, concentrations may also be varied depending upon the amount of correction required. For instance, variables in the prints to be treated must be considered such as the paper type and weight, the thickness and composition of the coating, the mechanical flexing if any, and the drying operation subsequent to the curl prevention treatment. Consequently, it may be desirable to use a concentration as high as 50% plasticizer or a concentration as low as 5% depending upon the application.

In view of the prior art which shows conventional plasticizers or "print flatteners" to be glycols, it has been considered required that a chemical used as a print flattener have hydroxyl groupings on the molecule and be hygroscopic. Consequently, it was completely unanticipated that the long chain ethers which we have used would be operative for this purpose. We have further discovered that these long chain ethers become less hygroscopic as the general length increases. Also we have discovered that the detrimental effects caused by the presence of hydroxyl radicals such as excessive gelatin shrinkage at low relative humidities are avoided.

It will be seen from the proceeding description that through our method, we have been able to produce photographic prints which have handling characteristics not normally found. It should be understood, of course, that the scope of this invention is not confined to the two chemical compounds referred to in the examples. Other long chain, non-hygroscopic materials known to be gelatin plasticizers can be used according to our invention, such as ethers having a chemical composition $RO(CH_2CH_2O)_nR'$ wherein R and R' are alkyl groups an n is a number larger than 2 but less than 135. Examples of compounds of this type in addition to tetraethylene glycol dimethyl ether and diethylene glycol diethyl ether are dimethoxy polyethylene glycols, diethoxy polyethylene glycols, dimethoxy polypropylene glycols, and diethoxy polypropylene glycols.

We claim:

1. A process for treating photographic paper carrying a gelatin layer to eliminate post processing curl, comprising impregnating the gelatin layer with a long chain non-hygroscopic organic ether having a chemical composition

$$RO(CH_2CH_2O)_nR'$$

in which R and R' are alkyl groups and n is a number between 2 and 135.

2. A process according to claim 1 in which the long chain ether is selected from a group consisting of tetraethylene glycol dimethyl ether and diethylene glycol diethyl ether.

3. A process for treating a paper based gelatin layer to remove the curl caused by the shrinkage of the gelatin, comprising applying a gelatin plasticizer which is a long chain organic ether having a chemical composition $RO(CH_2CH_2O)_nR'$ in which R and R' are alkyl groups and n is a number between 2 and 135.

4. A process according to claim 3 in which the long chain ether is selected from a group consisting of tetraethylene glycol ether and diethylene glycol diethyl ether.

5. A process for eliminating post processing print curl from photographic paper carrying a gelatin layer, comprising impregnating the surface of the print with a water solution of a plasticizing agent selected from the group consisting of tetraethylene glycol ether and diethylene glycol diethyl ether, and drying the print in an atmosphere of low relative humidity.

6. A process as described in claim 5 wherein the curl control treatment is applied following the washing step in conventional photographic print processing.

7. A process according to claim 1 wherein the ether is contained in a solution in which the ether concentration is between 10%, and 20% by weight.

8. A process according to claim 7 wherein the solution applied comprises water and ether.

9. A process according to claim 5 wherein the ether concentration is between 10% and 20% by weight.

10. A process according to claim 9 in which the prints are soaked for at least 15 minutes in the ether solution.

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No references cited.