The present invention relates to photographic material and more particularly to the base material supporting a photosensitive coating, and this application is a continuation in part of our prior application Serial Number 861,764, filed Dec. 24, 1959, now abandoned.

There has been a problem in obtaining a suitable material for photographic prints, due to the fact that the base material would frequently react with the photosensitive emulsion, causing the photosensitive emulsion to deteriorate. Consequently, photosensitive materials have had a relatively short shelf life.

An object of the present invention is to provide an impregnated for relatively inexpensive base material to render the base material suitable for supporting a photosensitive material.

Another object is to provide a photographic sheet having a relatively inexpensive porous base.

A further object is to provide a treatment for paper to reduce hygroscopic properties and prevent physical changes caused by atmospheric moisture and to render a base paper chemically inert.

Another object is to bind impurities in the paper in animal glue sizes therein from migrating into a photosensitive coating on the paper.

A further object is to provide a paper of improved strength and improved properties with respect to moisture content therein.

Another object is to provide a treatment for inexpensive paper to render it suitable for photographic emulsions and provide long shelf life for a sensitized photographic paper made therefrom.

More particularly, the present invention provides for the treatment of paper made from any suitable material such as 100% rag, sulfate, or sulfite or combinations of rag and sulfate and sulfite papers, which base paper is impregnated and/or sized with animal glues and organic or inorganic glues and sizes which will provide free or reactive hydrogen groups for cross-linking when combined with suitable resin materials. A suitable resin material has been found to be epoxy resins in which the oxygen atom is connected to two adjacent carbon atoms whereby such oxygen atoms may react with free hydrogen groups and particularly the free hydrogen in the amino groups in the animal glues and sizes thereby forming a resinous bond and rendering the sizes non-reactive and binding any objectionable constituent materials or impurities so that a coating of photosensitive material such as a coating of silver halide gelatin emulsion will not be adversely affected by the paper or the various constituent materials in the paper.

In the manufacture of paper according to the present invention the fibers are beaten together in a heater where the animal glues and/or sizes are added. The resulting paper may have many pores or interstices therein and the paper may be sufficiently porous to receive further treatment.

One paper used is known as American Writing Paper Corporation 404/407 100% cotton fiber furnish paper having an internal size of common resin (abietic acid), soap and aluminum stearate (referred to as papermakers' alum) which has been surface sized with 100% animal-hide glue by continuously passing a web of the paper through a tank of the glue solution and removing the excess glue solution by pressing the web of paper with the glue thereon between doctor rollers which remove the excess glue leaving a thin coating of glue which does become impregnated into the paper web. This animal hide glue (organic colloid of protein derivation) is high grade having a jelly-strength value of 315 bloom grams (measurements according to National Association of Glue Manufacturers). The glue is dried in the usual way and 1 to 3% of glue by weight relative to the weight of the sized paper is retained in the finished sized paper.

Another paper known as 244 Dalton Roll Bond manufactured by Crano & Co., 100% cotton fiber furnish, with an internal size of aluminum stearate is similarly surface sized with 100% high grade animal glue with 2 to 5% by weight of the glue relative to the weight of the finished sized paper being retained in the finished sized paper.

The papers used are transparent or translucent similar to tracing paper so that developed images in photographic emulsions applied to the paper can be duplicated by contact printing.

After the paper has been surface sized to incorporate the animal glue therein, a further treatment according to the present invention is the addition of a solution of an epoxy resin such as that trade name of "Epon," which is mixed with a suitable solvent. The web of paper is passed through a bath by complete immersion in a very liquid solution of epoxy resin so that the paper is completely impregnated, the excess resin being removed by any suitable means such as rollers, air bar, scraper, or the like and returned to the bath. Thereafter the resin retained in the paper is cured. The solvent for the resin is evaporated from the web of paper by passing the web through an oven or the like, the heating in the oven removes the solvent from the epoxy resin and assists in completing the cure of the epoxy resin impregnated paper. In curing, the resin reacts with the free hydrogen in the animal glue such as reacting with the hydrogen in the amino groups. The amino groups in the animal glue serve the function which had previously been served by curing agents such as ethyleneimide, diethylenetriamine or other curing compounds for the epoxy resin. These known curing agents for epoxy resins are toxic, unpleasant and irritating to workers, and therefore are objectionable to use. The present invention avoids the need and the expense for any curing agent.

The present invention avoids these curing agents and avoids the toxic effect, the unpleasant odors and the skin irritations caused by these previously used curing agents for epoxy resins. The treatment of the paper web according to the present invention renders the paper non-reactive so that a subsequent coating on the epoxy resin impregnated animal glue sized paper will result in a stable product which will maintain its useful life for an extended period of time.

Another unexpected and obvious advantage of applying the epoxy resin directly to the paper without a curing agent is that the viscosity of the epoxy resin solution is kept in the desired liquid condition for the desired degree of penetration into the paper and there is no setting of the epoxy resin until the epoxy resin is in place within the interstices of the paper where the setting reaction with the animal glue occurs. Therefore the liquid epoxy resin solution applied to the paper in accordance with the present invention remains in constant uniform liquid condition during the entire application of the epoxy resin to the paper assuring uniform impregnation and treatment of the paper.

The epoxy resin treating process according to the present invention therefore can be discontinued at any time by merely removing the paper from the solution of epoxy
The epoxy resin remaining in the immersion bath will not set and will remain liquid for use at a later time since no setting or curing agent is present in the resin solution.

The photographic emulsion coating can be applied by a meniscus coating method with a roller to a continuously moving web of reacted epoxy resin impregnated paper. Since the epoxy resin and the animal glue sizes in the paper web have reacted, there should be no tendency toward further reaction which could adversely affect the photographic emulsion. The photographic emulsion may be in the form of a silver halide gelatin emulsion, a dichromate emulsion, an emulsion hardenable by means of diazido compound, or the like. Suitable liquid formulations having the desired low viscosity for impregnating the web of paper have been found to be:

**Formulation examples**

1. Epon 1001 40-45
   Toluene 30-40
   Ethyl acetate 5-10
   *Percent*  
   *Grams*

2. Xylene 30  
   Ethyl acetate 45  
   Epon 1001 30  
   *Percent*  
   *Grams*

3. Toluene 35  
   Xylene 35  
   Epon 834 25  
   Epon 828 15  
   *Percent*  
   *Grams*

Epon is a trade name of an epoxy resin composition and is described in Technical Publication SC–52–51 of the Shell Chemical Corporation published in 1952. The chemical structure of the Epon resin is indicated on page 7 of this publication to be as follows:

\[ \text{Epon } 1001, 834, \text{ and } 828 \text{ have the same chemical structural formula with only the "n" varying and have properties as indicated in the table on page 6 of the same publication.} \]

Epon 1001 has a melting point between 64 and 76 degrees centigrade and an epoxy equivalent of 450–525. Epon 834 is a liquid having a melting point between 20 and 28 degrees centigrade and an epoxy equivalent of 225–590. Epon 828 is a liquid with a melting point between 8 and 12 degrees centigrade and an epoxy equivalent of 190–210.

A suitable subbing for the photo-sensitive emulsion is found in Scanlan Patent 2,495,661 as follows:

<table>
<thead>
<tr>
<th>Percent</th>
<th>Acetic acid, 2,500 cc.</th>
<th>H₂O₂, 1,500 cc.</th>
<th>Acetone, 3,000 cc.</th>
<th>Ethyl alcohol, 3,000 cc.</th>
<th>Formaldehyde, 100 cc.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>24.7</td>
<td>14.2</td>
<td>28.4</td>
<td>28.4</td>
<td>.95</td>
</tr>
</tbody>
</table>

A suitable photosensitive emulsion is found in Neugebauer et al. Patent 2,656,271 as follows:

<table>
<thead>
<tr>
<th>Percent</th>
<th>Glue, 5 liq. oz.</th>
<th>AgNO₃, 9 liq. oz., 3.07 oz. solid</th>
<th>KCl, 9 liq. oz., 1.43 oz. solid</th>
<th>H₂O₂, 77 liq. oz.</th>
<th>(NH₄)₂CrO₇, 9 liq. oz., .39 oz. or 11 g. solid</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5.8</td>
<td>3.5</td>
<td>1.7</td>
<td>89.</td>
<td>.45</td>
</tr>
</tbody>
</table>

It will be evident that other naturally occurring colloids such as glue, casein, albumen, with chromic acid usually added in the form of chromic salts may be used in the subbing and photosensitive coatings.

From the above description, it will be apparent that applicants have taken a transparentized paper which has been surface sized with a solution of an animal glue so that the glue sizing enters the interstices and pores of the paper and applied a solution of epoxy resin to that sized paper by immersion of the paper in a very liquid bath of the epoxy resin causing the epoxy resin to enter the interstices of the paper. No setting reaction of the epoxy resin can occur until the resin is in situ in the paper in contact with the animal glue and the solution of epoxy resin can therefore be made of the most desirable viscosity for entry into the pores and interstices of the paper to get the desired results. The setting action occurs only after the resin is in place in the paper and this advantageous result can not be obtained where a separate curing agent is added to the resin.

Although all of the actions and effects are not thoroughly understood, it is believed that impurities in the paper or in the glue which may not be combined with the resin are effectively held in place and surrounded by set epoxy resin so that such impurities do not adversely affect a photosensitive coating on the paper.

The paper with or without the photosensitive coating thereon may have images drawn thereon so that photocopies may be altered and both positive and negative photocopies can be made.

It will be seen that applicants have provided an inexpensive base paper and photosensitive product for use in reproduction and it will be apparent that variations can be made within the valid scope of the claims.

What is claimed is:

1. A non-reactive paper for use as a photographic base comprising a 100% cotton fiber paper sized with an animal glue leaving approximately 3% of the glue in the paper based on weight of the sized paper, epoxy resin of the general structure:
3,220,845

wherein \( n \) may vary within a range where the melting point is generally between 8 and 76 degrees centigrade and the epoxide equivalent is generally between 190 and 590 and without further catalyst, said resin reacted with the glue rendering the sized paper substantially non-reactive with photographic sensitive coatings applied to the paper.

2. A sheet material suitable for receiving photosensitive coatings comprising a good quality fibrous material sized with animal glue and reacted with epoxy resin of the general structure:

\[
\begin{align*}
\text{CHO} & \text{CH}_2 - \text{CH}_2 \text{O} - \text{CH} - \text{CH}_2 \text{O} - \text{CH} - \text{CH}_2 \text{O} - \text{CH} - \text{CH}_2 \text{O} - \\
\text{CH}_3 & \text{O} - \text{CH} - \text{CH}_2 \text{O} - \text{CH} - \text{CH}_2 \text{O} - \text{CH} - \text{CH}_2 \text{O} - \text{CH} - \text{CH}_2 \text{O}.
\end{align*}
\]

wherein \( n \) may vary within a range where the melting point is generally between 8 and 76 degrees centigrade and the epoxide equivalent is generally between 190 and 590 and without further catalyst, said resin impregnated within the sheet material subsequent to the animal glue sizing of the sheet material to cause the animal glue and epoxy resin to combine forming a product which renders the animal glue and the sheet material substantially non-reactive with photographic coatings applied to the paper.

3. A paper sheet for receiving a photographic coating on at least one surface thereof without adverse effect on the photographic coating comprising a paper sheet having an animal glue sizing impregnated within said at least one surface thereof, and in which the said at least one surface has been thereafter treated with a very liquid and penetrating solution of an epoxy resin free of a curing agent, said resin being of the general structure:

\[
\begin{align*}
\text{CHO} & \text{CH}_2 - \text{CH}_2 \text{O} - \text{CH} - \text{CH}_2 \text{O} - \text{CH} - \text{CH}_2 \text{O} - \text{CH} - \text{CH}_2 \text{O} - \\
\text{CH}_3 & \text{O} - \text{CH} - \text{CH}_2 \text{O} - \text{CH} - \text{CH}_2 \text{O} - \text{CH} - \text{CH}_2 \text{O} - \text{CH} - \text{CH}_2 \text{O}.
\end{align*}
\]

wherein \( n \) may vary within a range where the melting point is generally between 8 and 76 degrees centigrade and the epoxide equivalent is generally between 190 and 590 and without further catalyst, and which solution of epoxy resin free of a curing agent penetrates said at least one surface of the paper sheet into effective intermingling with the animal glue with the epoxy resin being cured by combination with the amine groups present in the animal glue rendering the animal glue non-reactive, the cured epoxy resin effectively coating objectionable impurities in said paper sheet adjacent said at least one surface thereof so that said at least one surface of the paper sheet may receive a photographic coating.

4. The invention according to claim 3 in which a silver halide emulsion photosensitive coating covers said at least one surface of said paper sheet.

5. The method providing non-reactive paper base for photographic sheets to be subsequently coated with a photosensitive coating comprising, treating a base paper sheet which has been sized with animal glue in the manufacture thereof with an epoxy resin, of the general structure:

\[
\begin{align*}
\text{CHO} & \text{CH}_2 - \text{CH}_2 \text{O} - \text{CH} - \text{CH}_2 \text{O} - \text{CH} - \text{CH}_2 \text{O} - \text{CH} - \text{CH}_2 \text{O} - \\
\text{CH}_3 & \text{O} - \text{CH} - \text{CH}_2 \text{O} - \text{CH} - \text{CH}_2 \text{O} - \text{CH} - \text{CH}_2 \text{O} - \text{CH} - \text{CH}_2 \text{O}.
\end{align*}
\]

wherein \( n \) may vary within a range where the melting point is generally between 8 and 76 degrees centigrade and the epoxide equivalent is generally between 190 and 590 and without further catalyst, said resin being of thin consistency in an aqueous solution penetrating the pores of the paper base and intermingling with the animal glue in intimate association whereby the epoxy resin is cured by the reaction with the animal glue in situ within the pores of the paper thereby coating impurities and preventing further activity of the animal glue and impurities with a photosensitive coating to be subsequently applied.

6. The method according to claim 5 including applying an emulsion to the treated paper.

References Cited by the Examiner

UNITED STATES PATENTS

2,880,116 3/1959 Alps et al.
2,882,250 4/1959 Baker
2,913,356 11/1959 Schroeder

FOREIGN PATENTS

586,856 11/1959 Canada.

OTHER REFERENCES


NORMAN G. TORCHIN, Primary Examiner.