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DIAZOTYPE SENSITIZED PAPERS HAVING
CELLULOSE ETHER SIZING

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1

This invention relates to photosensitive papers and more particularly to a method of improving the uniformity of penetration of the sensitizing material into the paper or other porous support.

In the process of sensitizing a sheet of paper or other similar porous material used for a support with a sensitizing solution for the production of a ferro print or blueprint, a diazotype layer or a Van Dike type sensitized layer, it is necessary to treat the support in such a way that it has extremely uniform absorption characteristics. In the case of those papers which are generally employed in the production of, for instance, diazotype layers, this uniformity of absorption has been accomplished by imparting a surface sizing to the paper. For this purpose, there is commonly employed starch or a modified or converted starch, such as enzyme-hydrolyzed or chlorinated starch. This starch sizing is prepared by cooking to a smooth consistency and, if desired, adding materials to control the pH during conversion, such as calcium carbonate. In addition, soaps may be added as, for example, sodium oleate, in order to increase the viscosity. Such a starch sizing is applied by dipping the paper off the paper machine or just prior to the rewinder of the paper machine into the starch bath, after which the paper is dried with a gentle heat. This process may be repeated in order to build up a relatively thick surface sizing and the thus highly sized paper is then altered by subsequently super-calendering to impart a smooth finish and minimize the tendency for rapid absorption. If the paper or other such porous material used as the support for a photosensitizing layer is not finished in this manner, it has been found that the sensitizing solution will break through, forming pinholes or speckles and thus impair the uniform photographic effect.

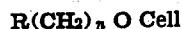
It has been found, however, that papers which have been highly sized with a surface sizing, such as is imparted by the above treatment, must be coated with the sensitizing solution at relatively slow speeds and that very concentrated solutions must be used or the resulting penetration is not deep enough to allow for the production of images having satisfactory visual density after the photosensitized material has been exposed and developed.

I have found that by adding to the photosensitizing solution or by substituting certain cellulose ethers for part or all of the surface sizing material, such as starch, photosensitized coatings may be obtained on paper or other porous material support having highly desirable improved properties.

2

For instance, it is possible to use low temperature drying after application of the sensitizing solution and thus promote deep penetration of the sensitizing solution without danger of obtaining non-uniformity of the coating. The subsequently produced images will then be obtained in deep colors or colors of greater visual density, thereby giving the images improved sharpness, clarity and definition. The diffusion of the photosensitizing components into the fiber of the paper is also somewhat minimized. It is also possible to coat the sensitizing solution on the paper support with an increased rate of application.

The cellulose ethers which I have found produce these desirable results when added to the photosensitizing solution for application to the paper support or when substituted for part or all of the starch surface sizing are members of the group represented by the following formula:



wherein R is a member of the group consisting of OH and COOH radicals, n is one of the integers 1, 2, 3 and 4, and Cell represents a cellulose nucleus.

Specific examples of such cellulose ethers are hydroxymethyl cellulose, hydroxyethyl cellulose, carboxymethyl cellulose, carboxyethyl cellulose, hydroxypropyl cellulose and hydroxybutyl cellulose.

In carrying out this process, the cellulose ether may be used to pretreat the paper as a surface sizing in the same manner as is outlined above in applying the usual starch sizing. The paper is then dried and the photosensitizing solution applied.

In another modification, the cellulose ether may be coated on the finished paper, the excess of the cellulose ether solution removed and the sensitizing solution applied without any intermediate drying.

In still another modification, the components of the photosensitizing solution may be added to the sizing solution containing the cellulose ether and the resulting solution used as a surface sizing of the paper as it comes off the paper machine or as a coating or additional sizing for the finished paper. Also, as indicated above, the cellulose ether may be added to the photosensitizing solution and this applied in any of the methods generally used for the coating of a photosensitizing solution onto paper.

In practice, the composition of the size used when the cellulose ether is to be added to the surface sizing may vary over a wide range, de-

pending upon how thick a surface sizing is desired. The total sized content may range from about 1-10% by weight in solution. Cellulose ethers produce very viscous solutions even in low concentration and, accordingly, are used in fairly small amounts. I have found it unnecessary to employ amounts exceeding 2% in order to obtain a satisfactory surface sizing. In general, the preferred range of cellulose ethers in the sizing bath is from 0.5 to about 1%. Where other sizing materials, such as starch, are employed with the cellulose ethers, the concentration of such additional sizing materials may vary from about 3 to 9.5%. When the cellulose ether is added to the photosensitizing solution, concentrations of about 1% have been found to increase the viscosity of the coating solution to a sufficient degree to give uniform penetration and minimize the effect of excessive penetration into pin holes or other open places in the paper.

Although it is preferable to employ a paper stock which has already been given a beater size and calendering or in addition already possesses the usual surface starch sizing, nevertheless it has been observed that good results may also be obtained even on papers of more open or porous structure than those so treated, when the cellulose ethers of this process are used either as a surface sizing or as an addition compound to the photosensitizing solution. Accordingly, it is to be understood that this invention is not limited to the use of any particular type of paper. Furthermore, instead of employing paper as the base or support, the cellulose ether size may also be applied to cloth.

The photosensitized layer or coating may be produced on the papers treated in accordance with this invention by applying any of the usual photosensitizing solutions known to the art for the production of blueprints, Van Dyke types or diazotypes. However, the process will be particularly described in conjunction with the diazo-type light sensitive layers since paper treated in accordance with the process of this invention is particularly adaptable to the diazo sensitizing process. Any combination of diazo compounds and coupling components may be used in the sensitizing solution for the purpose of producing any desired shade in the developed image. The coupling components necessary to develop the azo dye image in the diazotype process may be incorporated in the sensitizing solution with the diazo compound in accordance with the well known two-component or dry development process or the coupling component may be used in a separate alkaline developing solution, in which case the diazo compound is the only dye component present in the sensitizing solution in accordance with the well known one-component or wet development process. If the two-component or dry development process is used, then the sensitizing solution may also contain stabilizing compounds, such as tartaric acid, thiourea and the like. Using paper which has been treated with the cellulose ethers of this process in either of these diazo-type processes, improved results are obtained regardless of the particular diazo sensitizing solution employed. Evenness of penetration of the sensitizing agents is obtained; voids and deep spots are substantially overcome, insofar as their tendency to create unevenness of penetration is concerned; the substantivity and visual density of the dye image is markedly increased; the diffusion of the dye components into the base is minimized; and it is possible to employ low temperature in

drying of the sensitizing or coating solution after application to the paper in order to obtain deeper penetration without accompanying non-uniformity.

The following examples will serve to further illustrate my invention, it being understood that they are merely illustrative of the best manner of carrying out the invention and are not in any way limitations on its scope. Parts are by weight.

Example 1

A warm sizing bath is prepared by dissolving in water and cooking the necessary amount of chlorinated starch to produce a 4% solution. To this solution there is added 1% of hydroxyethyl cellulose. The resulting solution, while warm, is then applied to the surface of a length of paper in any conventional way and the surface size produced thereon is then air-dried. A satisfactory method of applying the size is to pass the paper between nip rollers which are immersed in the sizing solution. A coating of any desired thickness may be applied.

A sensitizing solution of the following composition is then applied to the sized paper:

14.0 parts of 2,1-diazo hydroxy naphthalene-5-sulfonic acid
7.0 parts by volume of concentrated hydrochloric acid
31.5 parts of nickel sulfate
4.9 parts of phloroglucine, and
20.0 parts of thiourea are dissolved in 1000 cc. of water.

This solution is spread on the sized paper by the usual coating method, using a doctor blade to insure a thin even coating. It is then slowly air-dried at a low temperature, exposed under a diapositive and the image developed by exposure to an atmosphere containing ammonia vapors. The resulting image was found to be very even and contrasty and contains no speckles.

Example 2

A warm sizing bath is made by dissolving and cooking the necessary amount of low viscosity enzyme-hydrolyzed starch to produce a 5% solution. To this solution is added 1% of hydroxymethyl cellulose. The warm solution is then applied to either one or both sides of the paper in the same manner as in Example 1.

A diazotype sensitizing solution is made up as follows:

10.5 parts of zinc chloride double salt of the diazo compound obtained from N-ethanol-ethylamino-4-aminobenzene
50 parts of citric acid
5 parts of 2,3-dihydroxynaphthalene
45 parts of thiourea
32.5 parts of the sodium salt of naphthalene 1,3,6-trisulfonic acid, and
6.9 parts of aluminum sulfate are dissolved in 1000 cc. of water.

This sensitizing solution is coated on the sized paper prepared as above by the usual coating method and in the same manner as indicated in Example 1. The light sensitive layer thus produced is then slowly air-dried at a low temperature and the dried sensitized paper exposed under a diapositive and developed by application of ammonia vapor. The image thus produced was of a deep uniform color having no speckles or high spots.

5

Example 3

An 0.5 to 1% solution of hydroxypropyl cellulose is prepared by dissolving the hydroxypropyl cellulose in water. This solution is then coated on a sheet of paper and dried. The thus treated paper is then sensitized with the same diazo sensitizing solution prepared in accordance with Example 2. The sensitized paper is then, after drying, exposed under a diapositive and developed by application of ammonia vapors. The results obtained are comparable in all respects with the results obtained in Example 2. By substituting hydroxybutyl cellulose for the hydroxypropyl cellulose of this example, similar results are obtained.

Example 4

A 1% solution of hydroxyethyl cellulose is prepared by dissolving the hydroxyethyl cellulose in water. This solution is then used as a surface sizing solution and is applied to a sheet of paper by passing the paper between nip rollers which are immersed in the sizing solution. The paper is then sensitized, prior to drying the hydroxyethyl cellulose sizing, by applying thereto a diazo sensitizing solution as follows:

9.8 parts of zinc chloride double salt of the diazo compound obtained from N-monoethylamino-2-methyl-4-amino benzene
50 parts of citric acid
6.5 parts of resorcinol
45 parts of thiourea
32.5 parts of the sodium salt of the naphthalene-1,3,6-disulfonic acid, and
6.9 parts of aluminum sulfate are dissolved in 1000 cc. of water.

This sensitizing solution is coated onto the undried but sized paper prepared as above by surface dipping the undried paper in a bath of the sensitizing solution as the paper emerges from the sizing bath. The paper is then slowly air-dried at a low temperature, exposed to a diapositive and developed by application of ammonia vapors. The image thus produced is very uniform and of a deep color which does not show any speckles or high spots.

As a modification of this procedure, the hydroxyethyl cellulose size may be applied to a finished paper prior to drying, that is, a paper which has been beater sized and then surface sized with a starch sizing, such as that used in Example 1, but has not been dried after application of the surface sizing. Such a paper treated by the hydroxyethyl cellulose size will be substantially free from voids and deep spots, will permit even penetration of the sensitizing chemicals and will yield dye images upon development which are very uniform and have good visual density.

Example 5

A diazo sensitizing solution is prepared as follows:

3 grams of 2,3-dihydroxynaphthalene-6-sulfonic acid

6

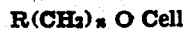
2 grams of p-diazo dimethylaniline
5 cc. of glycerine
2 grams of citric acid
2 grams of thiourea
2 grams of zinc acetate, and
1 gram of carboxymethyl cellulose is dissolved in 10 cc. of water.

This sensitizing solution is then spread on the surface of a paper which has not been surface sized and the excess of the sensitizing solution is removed in the usual manner by a doctor blade. The paper is then slowly air-dried at a low temperature. The dried sensitized paper is then exposed under a diapositive and developed by application of ammonia vapors. The image is produced in a deep color which is very uniform in its contrast and contains no speckles or high spots.

It will be obvious to those skilled in the art that various changes may be made in details of my invention as described in the foregoing specification and as particularly illustrated within the scope of the claims appended hereto without departing from the spirit of the invention.

I claim:

1. A diazotype sensitized paper coated with a sensitizing solution containing a light sensitive diazo compound as the sensitizing agent and pre-coated with a surface sizing comprising an ether of cellulose conforming to the general formula



wherein R is a member of the group consisting of OH and COOH radicals, n is one of the integers 1, 2, 3 and 4 and Cell represents a cellulose nucleus.

2. A diazotype sensitized paper coated with a sensitizing solution containing a light sensitive diazo compound as the sensitizing agent and pre-coated with a surface sizing comprising hydroxyethyl cellulose.

3. A diazotype sensitized paper coated with a sensitizing solution containing a light sensitive diazo compound as the sensitizing agent and pre-coated with a surface sizing comprising carboxymethyl cellulose.

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