Patented May 9, 1944

2,348,686

UNITED STATES PATENT OFFICE

2,348,686

PAPER

Clarence F. Van Epps, Lockport, N. Y., assignor to The Lauxite Corporation, Lockport, N. Y., a corporation of New York

No Drawing. Application March 27, 1940, Serial No. 326,286

2 Claims. (Cl. 95—8)

The present invention relates to photographic printing papers as well as protective wrappers for films and light sensitized papers.

The principal object of the invention is to provide a sized paper which will be inert, i. e., substantially chemically inactive to deteriorate light sensitive emulsions and chemicals. Papers of this character have heretofore presented difficulties in that either the printing paper per se or the wrapper have affected the sensitized coating to injure the same. Such objections as desensitizing or hypersensitizing are substantially eliminated by employing an improved paper which is plasticized and provided with a resinous sizing. The paper prepared in accordance with this invention is inexpensive, permanent and reliable.

Another object of the invention is to provide a sized paper which will be free from curling. This facilitates the application of a continuous uniform coating of light sensitive material to the paper. Moreover, in using printing paper, the curling which usually attends washing and fixing and drying of the print is substantially reduced.

A further object of the invention is to provide a sized paper which will be relatively non-absorbent. This characteristic materially decreases the period required for processing which, as well known, may include several immersion treatments. For example, by reason of the present invention, the drying times are substantially shortened.

The sized paper of the present invention has a high wet strength, is water resistant, abrasion resistant and is plasticized so that it is flexible and may be folded or otherwise handled without cracking.

I have discovered that the aforementioned objects and advantages are obtained by sizing the usual or satisfactory papers with a synthetic resinous material. In some cases, a continuous surface film is produced, while in other cases the individual fibres of the paper web are coated with a continuous film of the sizing. In other cases, both conditions may be present. By sizing, I mean either a surface coating, or partial or complete impregnation, or both coating and impregnation.

The resinous material which is preferred is a urea formaldehyde condensation product. There is preferably included in the condensation product an acid or acid providing material which appears to perform the function of a catalyst in the case of aluminum sulphate, and to actually enter into the reaction in the case of zinc chloride. In some cases, both the aluminum sulphate and zinc chloride are included in the reaction product in critical proportions.

The use of resins prepared by the condensation of urea and formaldehyde in the absence of acid providing materials as sizing materials is impractical in the preparing of photographic papers and wrappings. This is true for two reasons; namely, (1) the necessity for a clear solution which can only be obtained by an objectionably long heating period and (2) the requirement that the final reaction product be infusible and insoluble, which again demands a commercially unfeasible heating period. Moreover, the use of the resin in the absence of a plasticizer creates an objectionable embrittled product.

It is known that urea formaldehyde resins may be rapidly condensed in the presence of catalysts and acid reacting materials, but as explained above, photographic papers and wrappings present distinct problems, one of the most important of which is the provision of a sizing which is inert to the light sensitive chemicals, i. e., is chemically inactive to deteriorate the chemicals. However, non-absorbency and freedom from curling are likewise highly desirable, as are the other characteristics recited above, for a satisfactory product.

It has never heretofore been recognized that a properly prepared and applied urea formaldehyde resin sizing would improve sensitized papers and protective wrappings.

Carefully controlled conditions are employed to produce a clear homogeneous solution of the urea formaldehyde reaction product which I find is necessary to provide a continuous homogeneous sizing on the paper. In explanation of this, the clear resinous liquor must be water soluble and controlled so as to be capable of dilution with large volumes of water without precipitation. The formation of any precipitate whatever would produce discrete particles and it is an important feature of the present invention that by providing a clear homogeneous resinous hydrophilic aqueous solution, a continuous sizing film is obtainable on the paper or the individual fibres. These attributes are thus seen to be important to insure that the paper will be uniformly sized and free of discrete resinous particles. In referring to a clear resinous solution, I mean one which retains its clarity on cooling, is free of precipitates or cloudiness when used (preferably in aqueous solution) as a sizing material at any desired temperature, and forms a final infusible, insoluble and transparent size

on the paper. The control conditions include the ratio of urea to formaldehyde, pH control, the temperature and time utilized to carry out the reaction, and the presence of the catalyst or acid providing material in amount critically regulated to insure a rapid reaction product and one which is inert to sensitized coatings.

In preparing a clear water soluble partial condensation product in accordance with the present invention, the formaldehyde is first neutralized with caustic soda to about pH 7 and then mixed with urea in suitable proportions for the intended purpose. The amount of the catalyst such as aluminum sulphate which is added is critical, and its inclusion may take place at several stages, for example: (*a*) the catalyst may be added to the neutralized Formalin before or immediately after the addition of the urea and the reaction with urea then carried out; (*b*) the reaction of the neutralized Formalin with urea may continue through an initial stage, e. g., boiling, for about five minutes after the reacting materials have attained the boiling point and then the catalyst is added; and (*c*) the urea and formaldehyde are permitted to react further than in (*b*) and until the reaction has proceeded to the point at which the desired clear liquid resinous product is obtained after which the catalyst may be added to effect the final setting of the sizing in the paper. The fundamental reactions involved in procedure *b* and to some extent in procedure *c* are apparently between methylolurea compounds and the catalyst.

In connection with the above processes, where the aluminum sulphate is added to the neutralized Formalin, the amount added is particularly critical. I have found it best to include a quantity of aluminum sulphate sufficient to reduce the pH of the neutralized Formalin to about between substantially 5 or 5.1 and 6.5. Where the aluminum sulphate is added for reaction with the methylol compounds, i. e. after the reaction has proceeded through an initial stage or at the completion of the formation of the liquid reaction product, the pH may be reduced as stated, or reduced further to about pH 4.5. In other words, with the three processes *a*, *b* and *c*, above mentioned, the tolerance increases in accordance with the extent to which the reaction has proceeded and the catalyst may be added in amounts up to about 1% based on the dry weight of the urea.

Paper prepared with a uniform and continuous sizing on the paper or fibres in accordance with this invention is compatible with and chemically inert to sensitized coatings; e. g., silver halides such as silver chloride and silver bromide, as well as to other sensitized emulsions, coatings and chemicals, such as are used for the making of brown and white prints, black and white prints, and in blue printing.

In the case of photographic papers, the emulsion is critically prepared and delicately balanced, and the present invention preserves this quality to the end that the prints will be true and reliable. In other words, densitization or hypersensitization are substantially avoided. The same conditions exist where sized papers, in accordance with this invention, are used in connection with chemicals or sensitized coatings for the manufacture of prints of the brown and white, black and white type or blue prints. Furthermore, the delicate sensitivity of the emulsion or light sensitive coating is protected against abrasion and deteriorating chemical action by wrapping films or papers on which the same is coated in sized papers prepared in accordance with this invention.

In general, the sizing solution is prapered by reacting urea such as the commercial straight crystalline product with formaldehyde such as 37% Formalin in ratios of urea to formaldehyde of substantial one mol to two mols up to substantially one mol to four mols. Paraformaldehyde and thiourea may also be used. The proportions may, of course, be slightly increased or decreased by varying conditions, but those just recited are of a preferable and commercially satisfactory range.

By way of example, 347 parts of 37% Formalin are neutralized to substantially pH 7 and there is then added about .03 part of aluminum sulphate to reduce the pH to substantially 5.1. Thereafter, 115 parts of urea are added to the mixture which is then brought to boiling and the boiling continued for about 40 minutes at substantially 208° to 210° F. At this point a clear solution is obtained which retains its clarity upon cooling and is suitable for sizing paper in accordance with this invention.

The clear resinous liquid is water soluble and may be diluted with water to a solution containing any desired percentage of resinous solids. Such aqueous solution is free of precipitates and is homogeneous.

The proportions given in the foregoing example may, of course, be varied. In some cases, with varying proportions, the heating time may be from one minute to five hours with the temperature between substantially 208° and 210° F.

I prefer to include a plasticizer desirably a water soluble plasticizer in the sizing composition. Polyhydric alcohols such as glycerine or one of the glycols, namely, mon-, di-, or triethylene glycol are useful. The plasticizer may be incorporated initially with the reaction constituents, or at any of the stages of reaction above referred to, but is preferably added after the water soluble liquid resinous reaction product is obtained, either before or after the same has been diluted with the water.

The liquid resinous sizing prepared according to the aforesaid example is now suitably diluted with water, e. g., to form an aqueous solution having about 5% resinous solids. The plasticizer in proper amount is incorporated therein and there is thus provided a suitable bath in which the paper may be immersed by drawing a continuous web of the same through the bath. This immersion treatment will be controlled in accordance with whether a surface coating is desired, or whether partial or complete impregnation is required in the final product. In some cases, the immersion treatment is conducted under pressure, and in other cases conditions of partial vacuum may be present. Also, intermittent pressure and partial vacuum treatment may be used to assure the proper sizing of the paper web. As explained above, there are cases where both a surface coating and a partial or complete impregnation are required, and the sizing operation will be conducted in the most expeditious manner to accomplish this result. The term "sizing" is, therefore, referred to in the claims as covering any of the several treatments just described.

While I have described incorporating the plasticizer in the sizing, the paper may be plasticized by applying the plasticizer directly to the paper either before or after the sizing operation al-

though it is preferred to add the plasticizer in the manner above set forth.

After the paper web has been tub-sized as above described, it is subjected to a suitable temperature, namely, about 240° F. for a few minutes, e. g., two or three minutes or until the sizing changes from the water soluble stage to a condition where it is water insoluble and infusible. The paper product so obtained is sized with the reaction product of urea, formaldehyde and aluminum sulphate and it is chemically inert to light sensitive coatings. Moreover, the sized paper is plasticized which is important in that paper for the purposes of the present invention must not crack when folded and must be flexible so that it may be rolled and also handled for packaging and printing purposes without deterioration of the paper or structural breakdown.

The paper has high wet strength and water resistance so that it does not undergo deterioration in the presence of aqueous liquids or treating materials. Moreover, and of particular importance, the continuous and uniform sizing of the paper aids in assuring that the light sensitive coating applied thereto will be present likewise as a continuous uniform coating. The same is true with other light sensitive coatings which are applied to the sized paper.

Another important characteristic of the invention is the decrease in absorbency which is imparted to the paper and this in turn greatly adds to the manufacturing efficiency in that excessively long drying periods which may, in some cases, also affect the chemical coatings, are avoided.

Furthermore, as above stated, curling is substantially eliminated and this facilitates the application of the emulsion or other light sensitive coating without trouble from wrinkles or conditions of curl interfering with the formation of a uniform continuous coating.

While I have referred above to the use of aluminum sulphate and this is the preferred acid providing material or catalyst, in some cases zinc chloride may be utilized as the acid providing material.

As an example of a sizing of the type in which zinc chloride is used, 1735 parts of Formalin (37%), 537 parts of urea and 65.8 parts of zinc chloride are heated for 30 minutes at 190° F. The Formalin was not neutralized and the zinc chloride was added directly to it producing a pH of substantially 5.2. The clear liquor obtained by the reaction was diluted and a suitably sized plasticized paper prepared as above described.

In connection with the several examples, it is, of course, understood that light sensitive emulsions and light sensitive coatings vary as to composition and reactivity. The delicate balance of the light sensitive emulsions or light sensitive coatings, may require variations in the conditions of preparation and proportions of the constituents of the reaction products above described and it is to be understood that it is within the scope of the invention to comprehend these modifications which may particularly take the form of different degrees of light sensitivity, as well as chemical activity with respect to the sizings. The sizings referred to in this application are prepared so that the paper will be of a character which will not effect desensitization or hypersensitization of the light sensitive chemicals. In this connection, there are cases where both aluminum sulphate and zinc chloride are employed in the reaction product so as to produce a paper which has the desired inert quality. Of course, the proportions of the reaction constituents and the acid reacting materials will be suitably controlled to give the desired result.

The term "light sensitive chemicals" mentioned in the claims is intended to cover emulsions such as silver halides as well as those chemicals and coatings of a light sensitive character which undergo photo-chemical action.

I claim:

1. Paper having a sizing of urea formaldehyde resin including up to about 1% aluminum sulphate based on the dry weight of the urea, and a light sensitive coating applied over said sizing, said sizing rendering the paper non-absorbent to water and non-curling in the presence of water and being chemically inactive to deteriorate the light sensitive chemicals of said coating.

2. Paper having a sizing of urea formaldehyde resin including up to about 1% aluminum sulphate based on the dry weight of the urea, said paper being plasticized, and a light sensitive coating applied over said sizing, said sizing rendering the paper non-absorbent to water and non-curling in the presence of water and being chemically inactive to deteriorate the light sensitive chemicals of said coating.

CLARENCE F. VAN EPPS.