UNITED STATES PATENT OFFICE.

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PHOTOGRAPHIC FILM.

SPECIFICATION forming part of Letters Patent No. 623,963, dated May 2, 1899.

Application filed August 5, 1898. Serial No. 687,766. (No specimens.)

To all whom it may concern:

Be it known that I, FRANK C. AXTELL, a citizen of the United States, residing at Short Hills, county of Essex, and State of New Jersey, have invented certain new and useful Improvements in Photographic Films, of which improvements the following is a complete specification and description, which will enable others to make and use the same.

This invention relates to that class of photographic films which consist of a pyroxylin base or support, which base or support is coated with a sensitive photographic emulsion, the approved methods for the manufacture of which are well understood by those skilled in the art.

The adaptation of pyroxylin films as supports for photographic emulsions in photography is of comparatively recent origin, and it may be stated in a general way that they were first manufactured and introduced commercially about nine or ten years ago. Since that time their manufacture and use have assumed important proportions. Notwithstanding the many advantages—such as lightness, flexibility, &c.—which these pyroxylin supports possess as compared with the glass plates which they replace, they possess certain disadvantages which are of such nature as to seriously interfere with their utility and value as supports for photographic emulsions. The most important of these disadvantages and that which has limited their use to a considerable extent is the fact well known to those who have employed these sensitive pyroxylin films that the photographic emulsions with which they are coated and for which they act as supports soon lose their "sensitiveness" as compared with the stability of the same emulsions when coated upon ordinary glass plates.

Pyroxylin (by which I mean the soluble variety used for the manufacture of fluid or solid compounds thereof) is of an unstable nature, and if such pyroxylin in a dry state is confined in a closed vessel for any length of time it becomes what is technically known as "acid." This development of acid is due to a decomposition of the pyroxylin itself or of certain impurities contained therein, which decomposition gives rise to the formation of nitrous acid or its homologues. This same decomposition of pyroxylin occurs when it is exposed to the atmosphere in a dry state; but in this case the development of acid and other decomposition products appears to be less rapid than when the pyroxylin is confined. It also occurs in pyroxylin compounds formed by dissolving soluble pyroxylin or nitrocellulose, together with camphor or other solid solvents, in a suitable menstruum and either spreading the solution upon the surface of glass or metal and allowing it to dry and then stripping the dry sheet from the surface or else by subjecting the mixture to mastication in hot rolls, pressing it into a cake, and cutting it into sheets or other forms. Manufacturers of compounds of pyroxylin—such as "celluloid," "xylonite," &c.—have given a great deal of time and attention to the prevention of this decomposition of their product by incorporating with the material certain substances which are known technically as "antacids"—that is, substances which will neutralize or decompose nitrous acid and the lower oxids of nitrogen—and by the use of such antacid substances they have succeeded in imparting chemical stability to the product.

A long series of experiments and tests has demonstrated that when sheets or films of pyroxylin material made in the most careful manner and protected against acid decomposition by the incorporation of an antacid substance therewith are coated with sensitive photographic emulsions and the coated films or sheets are preserved for a certain length of time the sensitiveness of the emulsion on such films or sheets as compared with the sensitiveness of the same emulsion coated on glass suffers a considerable deterioration, and this deterioration appears to be cumulative. Other tests and experiments have shown that this deterioration is due to the presence of acids in the pyroxylin film. The first indication of the deleterious action of the pyroxylin film on the emulsion is a loss of sensitiveness, by which the emulsion is rendered "slower." With the lapse of time this loss of sensitiveness is intensified. By further keeping, in addition to the loss of sensitiveness, the

emulsion upon development shows what is technically known as "fog"—that is, a lack of sharpness, detail, and contrast in the developed negative or positive, until finally the emulsion loses practically all sensitiveness and it is impossible to obtain an impression thereon when exposed in the camera in the usual manner.

It is well known to those skilled in the manufacture of gelatino-bromid photographic emulsions that contact with certain acids is fatal to the sensitiveness and other desirable qualities of such emulsions. A careful examination of the pyroxylin sheets and films used as supports for such emulsions failed with the employment of ordinary methods to show the presence of acids in the materials; but by the application of refined chemical methods it was demonstrated that all pyroxylin compounds without exception contained small quantities of nitrous acid in a free state, and it was further demonstrated that the deterioration of emulsions when coated upon such pyroxylin sheets or films was due to the action of these acids upon the emulsions. I have also attempted to overcome the deleterious action of the nitrous acid on the sensitive emulsion by adding antacid substances to the emulsion before coating the pyroxylin support therewith; but I found that this method did not protect the sensitive film against deterioration, because the acid liberated by the pyroxylin film was obliged to penetrate the sensitive emulsion in order to come in contact with the antacid substances contained in the latter. The object of the present invention is to overcome this action, and I accomplish this by coating the sheet or film of pyroxylin material with a solution of gelatin or other suitable substance, which solution contains an antacid—that is, a substance capable of neutralizing or decomposing nitrous acid, and thus rendering it harmless. The sheet or film of pyroxylin material thus prepared is then coated with the sensitive emulsion.

In applying my invention I prefer to proceed as follows: A solution is made consisting of gelatin dissolved in water containing an antacid substance and a certain proportion of glycerin to impart softness to the resultant film. In the place of glycerin I may substitute other substances, such as the various soluble gums, albumen, starch, arrow-root, &c.; but in practice either a hard gelatin or a mixture of gelatin and albumen is to be preferred. I would state that a very good proportion of antacid substance is about two per cent. to the weight of the gelatin or other equivalent vehicle.

I have found the following formula to be effective for my purpose in making the antacid coating mixture, although, of course, I do not confine myself strictly to the ingredients and proportions therein named: hard gelatin, ten parts; water, one hundred parts; glycerin, ten parts; methyl alcohol, pure, five parts; urea, 0.2 part. The sheet or film of pyroxylin material is then coated upon one or both sides with this antacid mixture and is allowed to dry, by which means the sheet or film of pyroxylin material is coated with an attenuated film or substratum of gelatin or other equivalent substance containing an antacid. The sheet or film of pyroxylin material thus prepared is then coated with a sensitive photographic emulsion.

In applying my invention I do not confine myself to the use of gelatin or albumen, as any of the above-named substances, as well as others, may be employed according to the properties which it is desired to impart to the substratum or coating. Neither do I confine myself to the use of any specific antacid substance. Many such antacid substances are known and used in the manufacture of pyroxylin compounds. Among these is urea or carbamide, which I have found to answer every requirement when employed in my process.

I have found that sensitive photographic emulsions when coated upon films or sheets of pyroxylin material prepared as above retain their sensitiveness and other desirable qualities for an infinitely greater length of time than similar emulsions coated upon unprepared pyroxylin materials, and it will be seen that the emulsion is protected against the deleterious action of the acid developed by decomposition of the pyroxylin through the interposition of the antacid coating or substratum.

I have found that the addition of glycerin to the antacid mixture is very beneficial. It possesses the property of retaining a certain amount of water in the film deposited by such mixture, thus enabling the antacid substance to react more quickly and completely with the nitrous acid than is the case when no glycerin is used, and consequently no moisture is present. It is a fact well known to chemists that the presence of water is generally necessary in order that a chemical reaction of this kind may occur quickly and completely.

I do not claim the use of pyroxylin sheets or films *per se* as supports or carriers for photographic emulsions; neither do I claim the use of urea or carbamide as an antacid substance in pyroxylin mixtures, as I am aware that a patent has already been granted for its use for that purpose.

What I do claim, and desire to secure by Letters Patent, is—

1. The process which consists in coating sheets or films of pyroxylin material with a mixture consisting of gelatin, glycerin, and a substance which neutralizes or decomposes nitrous acid, substantially as described.

2. A sheet or film of pyroxylin material coated with a mixture consisting of gelatin, glycerin, and a substance which neutralizes or decomposes nitrous acid, substantially as described.

3. A sheet or film of pyroxylin material hav-

ing a coating of a mixture of gelatin, glycerin, and a substance which neutralizes or decomposes nitrous acid, overlaid with a sensitive photographic emulsion, substantially as described.

4. The process which consists in coating sheets or films of pyroxylin material with a mixture consisting of gelatin, glycerin, and urea, substantially as described.

5. A sheet or film of pyroxylin material coated with a mixture consisting of gelatin, glycerin, and urea, substantially as described.

6. A sheet or film of pyroxylin material having a coating of a mixture of gelatin, glycerin, and urea, overlaid with a sensitive photographic emulsion, substantially as described.

FRANK C. AXTELL.

Witnesses:
S. M. COOLEY,
FREDERIC ADAMS.