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STABILIZATION OF NITROCELLULOSE
FILM BASE

Donald R. Swan and John M. Calhoun, Roch-
ester, N. Y., assignors to Eastman Kodak Com-
pany, Rochester, N. Y., a corporation of New
Jersey

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This invention relates to photographic film and more particularly to photographic film of the high-speed type. More particularly, it relates to the stabilization of nitrocellulose film base for this type of film.

For many years, nitrocellulose has served satisfactorily as a film base with the older, slower types of photographic emulsions. Nitrocellulose, however, decomposes slightly on long storage, particularly at high temperatures, and its decomposition products have been found to decrease somewhat the speed of modern high-speed photographic emulsions coated on nitrocellulose film base. This is true even though the film base be coated on both surfaces with thin layers of other materials, before the application of the emulsion, so that the emulsion never comes in direct contact with the nitrocellulose. In order to maintain the optimum keeping qualities of these high-speed emulsions, it has, therefore, been preferable to use cellulose acetate film base with them. However, as nitrocellulose film base has certain characteristic physical properties, it is often desirable to use it for films carrying high-speed emulsions if otherwise satisfactory.

An object of this invention is to stabilize nitrocellulose so that it can be used in film base to which high-speed photographic emulsions are applied. Other objects include the stabilization of nitrocellulose for other uses.

While certain stabilizers for nitrocellulose have been known, such as urea and diphenylamine, they are not satisfactory for use in high-speed films. Diphenylamine, for instance, which is widely used in smokeless powder, gives a very dark greenish brown color to the film base, and hence, is entirely unsuitable for use in a film base which must be transparent and practically colorless. Urea, while it stabilizes the nitrocellulose to some extent, does not decrease the loss of emulsion speed when the film is stored. Many other compounds have been tried in the course of our investigation, but most of them either failed to stabilize the nitrocellulose, or imparted color to the film base, or fogged or desensitized the emulsion during storage.

We have found that the following hydroxy aromatic compounds, when mixed with nitrocellulose, particularly for film base, stabilize the nitrocellulose, do not fog high-speed photographic emul-

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sions, and materially decrease the loss of speed of high-speed photographic emulsions coated on the film base as compared to the loss of speed of the same emulsions coated on nitrocellulose film base not containing the stabilizer:

p-Tertiary butyl phenol
p-Tertiary amyl phenol
p-Hydroxy phenyl acetic acid

For the usual composition it is satisfactory if the film base contains no more than 2% of the hydroxy aromatic compound listed to cause satisfactory stabilization. Any amount of the hydroxy aromatic stabilizer above 2% is superfluous. It is desirable that at least 0.4% of the stabilizer be employed, although proportions less than this have been found to give a stabilizing action. For instance, .1% of stabilizer imparts some stabilizing action, while .2% increases the effect, which effect is increased still more by further proportions of hydroxy aromatic stabilizer, ordinarily up to a percentage within the range of 0.4% to 2%.

The hydroxy aromatic stabilizer is incorporated in the nitrocellulose in the case of film base by adding it to a solution from which the film base is prepared. For instance, in the preparation of a nitrocellulose film base in the conventional manner by depositing a solution of film-type nitrocellulose and plasticizer in volatile solvent on a film-forming surface, the plasticizer is incorporated therein and, therefore, is uniformly distributed throughout the film base. For instance, cellulose nitrate sheeting, having a composition in accordance with our invention, may be prepared by dissolving 100 parts of nitrocellulose, having a nitrogen content of 11.8%, in a mixture of 380 parts of methyl alcohol and 20 parts of acetone, together with 5 parts of dibutyl phthalate and 1 part of stabilizer such as listed herein. A viscous solution or "dope" is formed thereby. This solution is then coated onto a film-forming surface such as ordinarily employed in the preparation of cellulose ester sheeting. The nitrate film is then cured at a temperature of 120 to 250° F. for a sufficient time to remove substantially all of the solvent therefrom. After this has occurred, the sheeting thus formed is removed from the curing chamber and rolled up so as to form a roll of cellulose nitrate sheeting. This material is

suitable for use as the base for photographic film. If the stabilizer is to be employed for stabilizing a nitrocellulose to be employed for plastic purposes, the stabilizer may be conveniently incorporated in the nitrocellulose by working the material on hot rolls so that the stabilizer may be mixed into the plastic and thus be distributed therethrough.

In the case of nitrocellulose lacquers, the stabilizer may be incorporated by dissolving it in the solution or lacquer having a base of nitrocellulose. Although our invention is adapted for stabilizing nitrocellulose generally, it is particularly adapted to stabilizing film-type nitrocellulose such as those having a nitrogen content of 11.4 to 12.2%, such as nitrocellulose prepared by the process described and claimed in U. S. Patent 2,118,275 of Talbot.

Nitrocellulose, when subjected to heat, storing, seasoning, or long exposure, discolors and forms nitrogen oxides. The stabilizer merely delays the formation of the nitrogen oxides so that in commercial use the nitrocellulose does not break down within the ordinary life of that material. When the stabilizer is incorporated in the nitrocellulose that material will withstand the effect of heat or exposure for a much longer period of time than is the case with nitrocellulose which has not been stabilized. The stabilizing ability of a material is measured by the amount of nitrous acid given off from the nitrocellulose film base containing the stabilizing material when compared with a nitrocellulose film base of like kind except that no stabilizing material is present. For instance, to determine the stabilizing efficiency there is taken a sample of the nitrate film base to be tested and a check sample of cellulose nitrate film base which does not contain stabilizing material, and these are both heated at a temperature of 250° F. for 1 hour. A small portion of the samples (such as 0.5 gm.) are then cut into pieces separately, placed in a clean, dry bottle, and a reagent consisting of acetic acid containing sulfanilic acid and α -naphthylamine hydrochloride is added. The bottle is then closed and heated to 80° F. for 24 hours and the solution is then decanted into a glass cell and the concentration of the red dye formed is determined in a photometer. The concentration of nitrous acid in each sample is then determined from a calibration curve. The stability factor is easily determined from the results obtained in testing the samples for nitrous acid content. For instance, if the stabilized sample contained $7 \times 10^{-4}\%$ of nitrous acid and the check sample contained $150 \times 10^{-4}\%$ of nitrous acid, the stability factor would be determined by subtracting 7 from 150 and dividing the remainder by 150 or the proportion of nitrous acid in the check sample and multiplying by 100 to obtain the per cent value, this figure giving the stability induced by the stabilizing agent upon the nitrocellulose.

We have found that in typical examples of the use of the hydroxy aromatic compounds that a high stability factor evidences itself. For instance, by the test just outlined, employing 1% tertiary butyl phenol, the stability factor was

found to be 92%. The same value was found for tertiary amyl phenol, while for p-hydroxy phenyl acetic acid a stability of 93% was obtained, using a stabilizer concentration of 1%.

Although the stabilizing method given herein is useful for nitrocellulose generally, it is particularly useful for film-type nitrocellulose having a nitrogen content from 11.4 to 12.2%, such as nitrocellulose prepared by the process described and claimed in U. S. Patent 2,118,275 of Talbot. It has been found that film base containing nitrate of this type will remain almost colorless and will not detrimentally affect high-speed emulsions in contact therewith, even though stored for long periods of time when 0.4 to 2% of one of the hydroxy compounds listed is incorporated therein. It was found that in accordance with the stability tests described herein using 1% amounts of the hydroxy and aromatic compounds listed, that stability factors on the order of 92% were obtained.

Ordinarily nitrocellulose photographic film base consists essentially of nitrocellulose and a small percentage of a plasticizer such as dibutyl phthalate or triphenyl phosphate. The plasticizer is usually present in an amount from 5 to 10%, although this may vary from 1% or 2% up to 20%, depending on the amount of plasticizer action which is desired. Our invention also contemplates such a composition of matter containing a stabilizing amount of one or a plurality of the hydroxy aromatic compounds listed. It is preferred that such a composition be made up, for instance, of cellulose nitrate having a nitrogen content of 11.4 to 12.5% and approximately 5% of plasticizer and .4 to 2% of a hydroxy aromatic stabilizing compound, the percentages all based on the weight of the nitrocellulose. Such a material is particularly adapted for preparing sheet suited for carrying photographic emulsions, particularly of the highly sensitized, high-speed type, such as the emulsions used in high-speed cine-negative film, "Plus X" film, and "Super XX" film, as well as photographic emulsions of ordinary speed.

What we claim and desire to be secured by Letters Patent of the United States is:

1. A composition adapted for the preparation of photographic film base essentially consisting of nitrocellulose and a stabilizing amount of a hydroxy aromatic compound selected from the group consisting of p-tertiary butyl phenol, p-tertiary amyl phenol, and p-hydroxy phenyl acetic acid.

2. A composition adapted for use in the preparation of photographic film base essentially consisting of nitrocellulose and as a stabilizer therefor 0.4-2 parts per 100 parts of nitrocellulose of a hydroxy aromatic compound selected from the group consisting of p-tertiary butyl phenol, p-tertiary amyl phenol, and p-hydroxy phenyl acetic acid.

3. A composition adapted for use in the preparation of photographic film base essentially consisting of nitrocellulose and a stabilizing amount of p-tertiary butyl phenol.

DONALD R. SWAN.
JOHN M. CALHOUN.