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PHOTOGRAPHIC DEVELOPER AND A PROCESS OF PHOTOGRAPHIC DEVELOPING

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6 Claims. (Cl. 95—88)

My invention relates to the art of developing photographic silver halide emulsions and more especially to the curing of a defect arising in particular when developing emulsions, on films or paper, which were kept in store beyond the normal period of time or which are exposed to the action of the developer either unduly long or at an unduly high temperature. In cases such as here referred to the images developed in the emulsion are likely to become foggy.

It is an object of my invention to provide means whereby this defect is cured without the tint of the images, and quite particularly those produced in silver chloride emulsions, being affected to any appreciable extent.

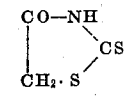
It is another object of my invention to provide a composition of matter possessing the properties of a developer and containing matter adapted to counteract fog formation in emulsions of the kind hereabove specified.

With these and other objects in view I will now proceed to describe the nature of my invention and the best way in which it may be performed.

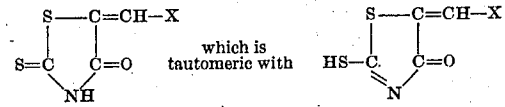
I have found that the products resulting in the condensation of 2-4-thioketothiazolidine with a non-basic cyclic aldehyde are powerful antifoggants, while hardly affecting the tint of the image developed, and this quite particularly in the case of silver chloride emulsions. I have further found that by admixing to a suitable silver halide developer a minute quantity, for instance of the order of 0.005 per cent, of a condensation product of the kind here in view, I am enabled to develop old silver halide and more especially silver chloride emulsions, or to develop any such emulsions during an abnormally long period of time or at an abnormally elevated temperature without incurring any risk of fog formation and decoloration.

I have found that this beneficial action of the condensation products mentioned above by far surpasses that of the imidazols and triazols.

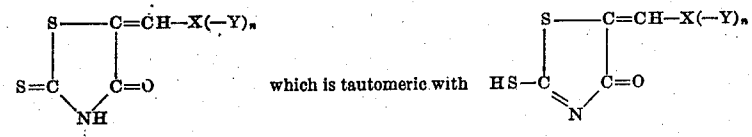
According to Richter-Anschütz' "Chemie der Kohlenstoffverbindungen" (12th edition), vol. 3, p. 143, the 2-4-thioketothiazolidine is constituted according to the formula



By condensation of this compound with a non-basic cyclic aldehyde there is formed a compound corresponding to the formula



wherein =CH—X is the residue of a non-basic cyclic aldehyde, while X may contain non-basic substituents. Such a substituted compound corresponds to the formula



wherein Y is a non-basic substituent of the nucleus X, while n is 1 or 2.

The following can be used as non-basic cyclic aldehydes, e. g.: benzaldehyde, nitrobenzaldehyde, salicylic aldehyde, protocatechuic aldehyde, brombenzaldehyde, anisaldehyde, heliotropine, benzaldehyde-sulphonic acid, cinnamic aldehyde, phenyl acetic aldehyde, furfurol, etc., etc. In case metaleptic benzaldehyde is used for condensation, it makes no difference on which carbon atom the substitution is found. Thus, for instance, the ortho-nitro-benzaldehyde is just as suitable as the meta-nitro-benzaldehyde or even a benzaldehyde which has two groups; for instance, a di-nitro-benzaldehyde. It is only important that the aldehyde shows no basic property, as for example the p-dimethylamino benzaldehyde which would lead to unsuitable products.

By adding for instance 1 part by weight of 2-thio-4-keto-5-ortho-hydroxybenzylidene thiazolidine to 20,000 parts of an ordinary metol hydroquinone developer I obtain a yellow colored liquid which can be used to develop old silver halide emulsions and quite particularly silver

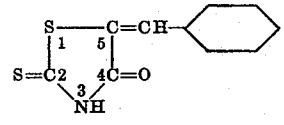
chloro-bromide paper without any risk of the images becoming foggy.

If the developer with the antifoggant admixed to it is allowed to stand, the yellow color will disappear almost entirely, depending on the content of alkaline substances in the mixture, however the antifoggant effect will not be diminished.

The percentage of the colored or decolored antifoggant in the developer may vary within wide limits, for instance between 1:5000 and 1:100,000. I have found a proportion of 1:20,000 to be particularly useful.

In practising my invention I may for instance proceed as follows:

1 mol. 2,4-thioketo-thiazolidine is boiled with 1 mol. benzaldehyde in about 10 mols glacial acetic acid for about 5 hours with reflux cooling. After cooling, brown crystals precipitate, which presumably have the following constitution:

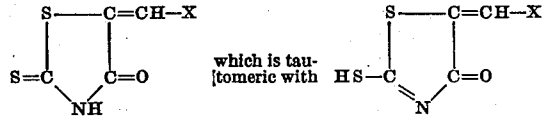


If of this 2-thio-4-keto-5-benzylidene-thiazolidine 0.05 gram is added to 1000 grams of an ordinary developer, old photographic paper which, if developed in the usual manner, would become foggy, can be developed free of fog in this developer. The effect on the colour of the picture is very slight. Even in developing at higher temperatures, as for instance 25° C. (77° F.), no fog will appear, not even if the process of developing is extended far beyond the usual period of time.

Various changes may be made in the details disclosed in the foregoing specification without departing from the invention or sacrificing the advantages thereof.

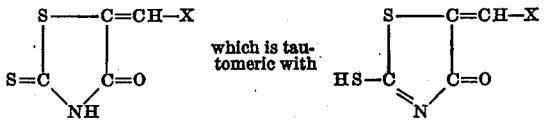
I claim:—

1. The mixture of a photographic silver halide developer with a compound corresponding to the formula



wherein =CH—X is the residue of a non-basic cyclic aldehyde, resulting from the condensation of such aldehyde with 2-thio-4-keto-thiazolidine.

2. The process of developing photographic silver halide emulsions which comprises exposing such emulsions to the action of a mixture of a silver halide developer with a compound corresponding to the formula

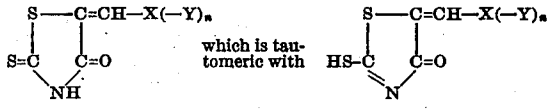


wherein =CH—X is the residue of a non-basic cyclic aldehyde, resulting from the condensation of such aldehyde with 2-thio-4-keto-thiazolidine.

3. The mixture of a photographic silver halide developer with 2-thio-4-keto-5-ortho hydroxybenzylidene-thiazolidine.

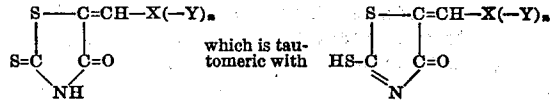
4. The process of developing photographic silver halide emulsions which comprises exposing such emulsions to the action of a mixture of a silver halide developer with 2-thio-4-keto-5-ortho hydroxybenzylidene-thiazolidine.

5. The mixture of a photographic silver halide developer with a compound corresponding to the formula



wherein =CH—X(—Y)$_n$ is the residue of a non-basic cyclic aldehyde, Y is a non-basic substituent in the nucleus X of said aldehyde, while n is an integer smaller than 3, said compound resulting from the condensation of such aldehyde with 2-thio-4-keto-thiazolidine.

6. The process of developing photographic silver halide emulsions which comprises exposing such emulsions to the action of a mixture of a silver halide developer with a compound corresponding to the formula



wherein =CH—X(—Y)$_n$ is the residue of a non-basic cyclic aldehyde, Y is a non-basic substituent in the nucleus X of said aldehyde, while n is an integer smaller than 3, said compound resulting from the condensation of such aldehyde with 2-thio-4-keto-thiazolidine.

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