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PHOTOGRAPHIC EMULSION

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4 Claims. (Cl. 95—7)

Our present invention relates to an improved sensitized photographic emulsion.

For enhancing the adhesion of the photographic emulsion to the film support (for example nitro cellulose or acetyl cellulose) there are used intermediate layers, so-called substrata or preliminary preparations which generally consist of feebly acid dispersions of protein substance in material which is a swelling agent for the support used. The sensitizers of the cyanine class which are now mostly used have as basic bodies the property of strongly coloring such preparations and substrata, so that in a disturbing manner a colored negative or positive is produced. This effect is particularly troublesome in the case of photomechanical films. The single acid dyestuff applicable as a sensitizer, namely erythrosin, has the property of coloring gelatin itself in such a degree that, even apart from the limitation of the sensitizing possibilities when there is only one dyestuff suitable only for a definite spectral zone the high coloring capacity is in many cases disturbing.

Our present invention has for an object the provision of sensitized photographic silver halide gelatin emulsions containing as sensitizers cyanine dyestuffs which consist of two heterocyclic nitrogeneous rings linked together by a methenyl chain, each of said rings containing a fatty acid radicle united in ω-position to the carboxyl-group of said radicle to the nitrogen atom of the heterocylic ring.

Another object of our invention is to provide photographic emulsions containing such acid cyanine dyestuffs the fatty acid radicles of which are identical.

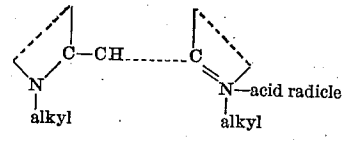
A further object of the invention is to provide photographic emulsions containing such acid cyanine dyestuffs the fatty acid radicles of which are not identical.

Other objects and advantages of our invention will be apparent from the following detailed description.

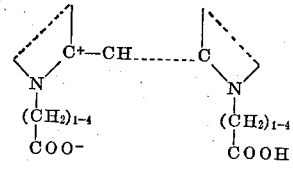
The preparation of the sensitizers of the present case is described in our co-pending application Serial No. 259,392, filed March 2, 1939.

These sensitizers are more easily washed out of the gelatin than are the corresponding basic dyestuffs, and in addition do not color the preparation. In many cases they display an enhanced sensitizing capacity as compared with the corresponding basic cyanine dyestuffs. Since not only symmetrical dyestuffs but also dyestuffs which in high degree are unsymmetrical having the above surprising properties may be used, various requirements in respect of intensity, range of sensitizing, stability to added substances and the like can be fulfilled by the dyestuffs. They are also, in respect of their solubility in the usual solvents after addition of a little organic or inorganic base, more suitable as an addition to an emulsion than are the known cyanine dyestuffs which in part are sparingly soluble, for example if they are used in the form of iodides or perchlorates or if in the form of more freely soluble chlorides or nitrates must be converted into these, which operation is accomplished only with difficulty and loss.

The dyestuffs differ from the known dyestuffs only in the simple fact that the nitrogen atoms of the hetero-rings do not attach the usual alkyl groups but fatty acid radicles united in ω-position to the carboxyl group to the nitrogen. While the known basic cyanines have a constitution corresponding with the following diagram



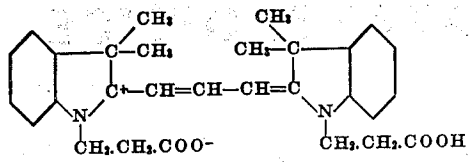
the new sensitizers have the constitution represented by the diagram



The fatty acids used may contain up to 5 carbon atoms. The fatty acid radicles united to the two nitrogen atoms may be the same or different. The new sensitizers, therefore, differ from the known cyanines merely in the nature of the N-substitution. This substitution may be performed in the case of all known cyanines, so that it is unnecessary to refer further to the individuals of these known cyanines. It was, however, quite surprising that these new dyestuffs should have at least the same sensitizing capacity as is possessed by the known basic cyanine dyestuffs, and that they should have in addition the aforesaid great advantages.

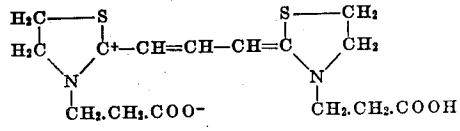
The following examples illustrate the invention:

Example 1.—A dyestuff of the following constitution:



sensitizes with a maximum at 605 mμ and shows a steep downward gradation towards the longer wave lengths. The dyestuff is produced, for example, from the condensation product of 1.1.2-trimethylindoline with β-iodopropionic acid by condensation with ortho-formic acid ester in pyridine.

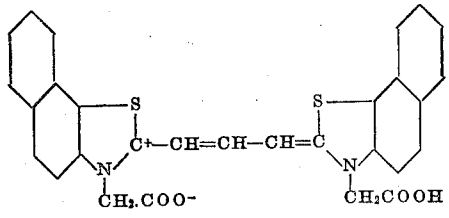
Example 2.—A dyestuff of the following constitution:



sensitizes with a maximum at 480 mμ. The dyestuff may be made, for example, in the following manner:

1 mol of 2-methylthiazoline is heated for ½ hour at 130° C. with 1 mol of chloropropionic acid, and the viscid mass is condensed with 3 mols of pyridine and 1 mol of orthoformic acid ester for one hour at 110° C.

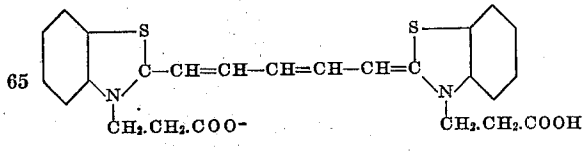
Example 3.—A dyestuff of the following constitution:



sensitizes with a maximum at 630 mμ. The dyestuff may be made as follows:

The condensation product of 2-methyl-β-naphthothiazole (from β-naphthylamine) with bromacetic acid is condensed for 2 hours in boiling pyridine with orthoformic acid ester. Dark needles separate from the solution which dissolve in water, on addition of some caustic soda lye, to a blue-violet solution having an absorption maximum at about 590 mμ.

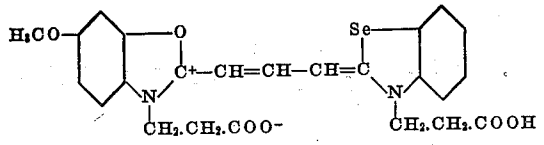
Example 4.—A dyestuff of the following constitution:



sensitizes with a maximum at 695 mμ, and may be made as follows:

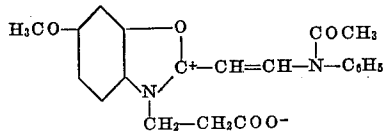
The condensation product from 1 mol of 2-methylbenzthiazole and 1 mol of β-iodopropionic acid is condensed with ½ mol of trimethinedianilide hydrochloride in methanol in presence of a base.

Example 5.—A dyestuff of the following constitution:



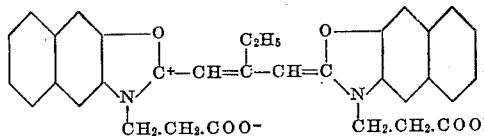
sensitizes with a maximum at 570 mμ, and may be made as follows:

1 mol of 2-methyl-6-methoxybenzoxazole is heated for 10 minutes at 170° C. with 1 mol of iodopropionic acid. The viscid mass thus obtained is heated for ½ hour at 100° C. with 3 mols of diphenyl formamidine and 1 mol of acetic acid anhydride; the intermediate product of the following constitution is produced:



This yellow product is condensed for one hour in boiling pyridine with 1 mol of the condensation product from 2-methylbenzselenazole and 1 mol of iodopropionic acid. The whole is poured into water and the dyestuff is precipitated by addition of dilute acetic acid. It may be recrystallized from methanol. It dissolves in water to which a few drops of piperidine have been added to an orange-red solution.

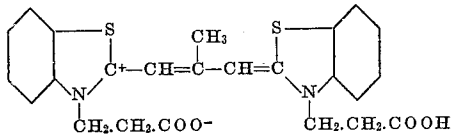
Example 6.—A dyestuff of the following constitution:



sensitizes at a maximum at 585 mμ. It can be made in the following manner:

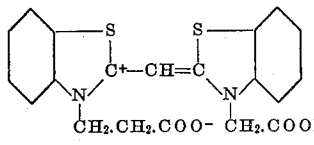
1 mol of 2-methyl-β.β'-naphthoxazole and 1 mol of β-bromopropionic acid are condensed together for one hour at 150° C. in the oil bath. The propionate obtained is further condensed with pyridine and 2 mols of S-ethylisothiopropionic acid anilide for 5 hours at 110° C.

Example 7.—A dyestuff of the following constitution:



has two sensitizing maxima, namely a maximum at 550 mμ and a principal maximum at 590 mμ. It is made from the condensation product of 2-methylbenzthiazole and β-iodopropionic acid by heating the condensation product for 3 hours at 100° C. with ethylortho-acetate in pyridine.

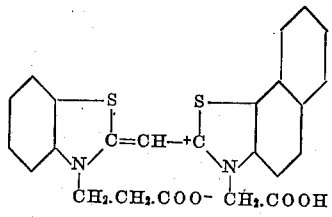
Example 8.—A dyestuff of the following constitution:



is produced by boiling for ½ hour a solution of 2-methylbenzthiazole bromoacetate and 2-

methothiobenzthiazole β-bromopropionate in pyridine. The dyestuff is yellow, and in silver chloride emulsion shows a sensitizing maximum at about 460 mμ.

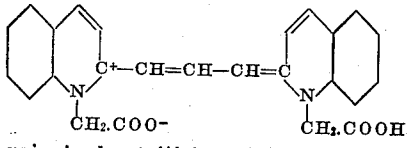
Example 9.—A dyestuff of the constitution:



has a sensitizing maximum at about 480 mμ. It may be made in the following manner:

1 mol of 2-methhthiobenzthiazole and 1 mol of β-iodopropionic acid are heated together for 20 minutes at 140° C. The liquid is then boiled for 1 hour in 10 mols of pyridine with the condensation product of 1 mol of 2-methyl-β-naphthothiazole and 1 mol of bromacetic acid (produced by heating for ½ hour at 130° C.).

Example 10.—A dyestuff of the constitution:



has a principal sensitizing maximum at about 645 mμ. It may be made by boiling the condensation product from 2 mols of quinaldine and bromacetic acid for ½ hour in a mixture of pyridine and methanol with 1 mol of iodoform and 3 mols of sodium ethylate.

We claim:

1. A photographic emulsion containing a cyanine dyestuff containing a fatty acid radicle united in ω-position to the carboxyl-group of said radicle to the nitrogen atom of each of the heterocyclic rings.

2. A photographic emulsion containing a cyanine dyestuff containing a fatty acid radicle united in ω-position to the carboxyl-group of said radicle to the nitrogen atom of each of the heterocyclic rings, said two fatty acid radicles being identical.

3. A photographic emulsion containing a cyanine dyestuff containing a fatty acid radicle united in ω-position to the carboxyl-group of said radicle to the nitrogen atom of each of the heterocyclic rings, said two fatty acid radicles being dissimilar.

4. A photographic silver halide gelatin emulsion containing a cyanine dyestuff containing a fatty acid radicle united in ω-position to the carboxyl-group of said radicle to the nitrogen atom of each of the heterocyclic rings.

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