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# WATER-MISCIBLE, STORAGE-STABLE AURAMINE BASE SOLUTION AND PROCESS OF PREPARING SAME

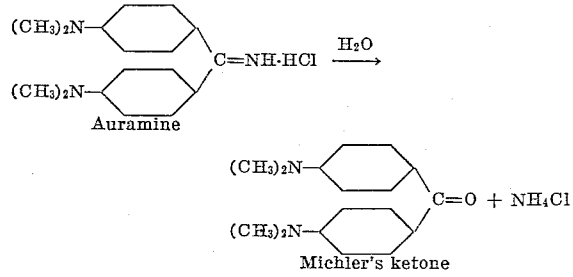
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This invention is directed to a novel composition of matter which furnishes readily an aqueous dye bath for use in the production of auramine-colored paper sheets or paper pulp.

The bright yellow dye known as auramine (C.I. Basic Yellow 2, C.I. 41,000) is the hydrochloride of 4,4'-bis-(dimethylamino)benzophenonimine. Its synthesis is described briefly in "The Chemistry of Synthetic Dyes and Pigments" (edited by H. A. Lubs), on page 246. It is generally sold in powder form for use primarily in the dyeing of paper from an aqueous solution of the color.

Auramine dissolves in cold water to the extent of about 0.5%. It has poor water solution stability, hydrolyzing quite rapidly in dilute aqueous solutions at slightly elevated temperatures according to the equation




Therefore, it is the practice to make up fresh dye solutions from the dye powder for each dyeing operation or short series of dyeings.

The hydrolysis of auramine in a dilute aqueous solution is readily observed by the turbidity which accompanies the formation of Michler's ketone, which is not a dye. Since the dyeing strength is proportional to the concentration of auramine base, any form or preparation of this dye which initially forms turbid solutions when dissolved in water is not desirable in the trade.

In addition, auramine in powder form is dusty to handle and dissolves slowly, particularly in water which approaches ice temperature as in winter-time dyeing operations.

Accordingly, it is a primary object of this invention to provide a novel and marketable form for the aforementioned dye which avoids the dusting troubles, is readily soluble in water, does not readily hydrolyze under the conditions of use, and has reasonably good storage stability to permit its packaging and handling in commerce.

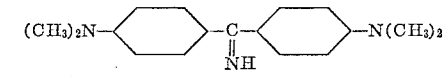
It is a further object to provide a process for preparing the heretofore described novel dye composition.

These and other objects will become apparent in the following description and claims.

Now we have found that all the aforegoing objects can be achieved by dissolving auramine base in essentially glacial acetic acid (or in acetic acid diluted by anhydrous hydroxyacetic acid), whereby to form a commercial solution containing up to 50% by weight of the color, calculated as base, and preferably, 35 to 40%, provided care is taken to exclude from the solution any substantial quantities of mineral acidity (e.g. HCl), water-soluble salts, auramine dye itself (i.e. the hydrochloride of the base) and Michler's ketone. By auramine base, of course,



is meant 4,4'-bis(dimethylamino)benzophenoneimine, i.e., the compound of formula




By water-soluble salts hereinabove, we mean alkali metal and ammonium salts of inorganic and organic acids (e.g. NaCl or ammonium acetate). By substantial quantities we mean quantities sufficient to produce a visible precipitate or turbidity in the acetic acid solution. Thus, mineral acid salts are essentially insoluble in glacial acetic acid and therefore will produce their own precipitate in the system; on the other hand, sodium acetate is soluble in glacial acetic acid to about 5%. Concentrations thereof, however, of about 5% have a salting out effect on the dye, auramine base acetate, whereas concentrations of 2% of sodium acetate have no ill effect on the stability of the system as judged by dye tests after storage for two months. Accordingly, exclusion of substantial quantities in this invention, in the case of salts soluble in acetic acid, means exclusion of quantities greater than about 3% by weight.

The upper limit in amount of anhydrous hydroxyacetic acid that may be mixed with glacial acetic acid is not critical, being determined by the physical characteristics desired for the dye solution. Since hydroxyacetic acid is a solid, and an object of this invention is to provide a dye solution which remains liquid at relatively low temperatures, a preferred upper limit for the hydroxyacetic acid is about 30% by weight of total solvent.

Water should also be excluded from the marketable concentrated solution, but its presence is not so critical as that of the other undesirable contaminants above mentioned, and quantities thereof up to 1.5% by weight based on the weight of the solution are not harmful to the objects of this invention.

We find that when constituted as above, the herein described novel composition is stable, as defined below, and does not hydrolyze appreciably when stored in a tightly closed container for two months at 35° C. Furthermore, it dissolves readily in water to produce therein the color, auramine base acetate, in concentrations varying from less than 0.04% (as dye base) to that of the original solution (say as high as 50%), and the diluted dye solutions are themselves stable for a sufficient length of time (say 8 or even up to 24 hours at room temperature) to permit their practical use in coloring paper pulp in the paper-making machine.

By contrast, aqueous solutions of only 0.5% concentration or less can be made from ordinary standard auramine powder (HCl salt), because of poor solubility, and these solutions become turbid after 2 to 3 hours. Thus the usefulness of such solutions is greatly impaired after relatively short periods of storage, a factor which renders them unsatisfactory for use in the trade.

For the purpose of this invention, two methods are available for testing the degree of hydrolysis suffered by a given composition in a given length of time. These are: (a) turbidity in dilute aqueous solutions and (b) dye test for dye strength.

The turbidity test is a qualitative but very sensitive test and is useful to detect trace amounts of hydrolysis. The dye test is useful to ascertain quantitatively the amount of dye which is lost by hydrolysis. In this test, the standard reference for strength is the dyeing on paper obtained from a freshly prepared dye bath containing a calculable amount of auramine base applied as auramine standard dye powder. For instance, a 10% weakness of a dyeing made from a sample of auramine base concentrated solution (of known initial dye content) compared

to the same amount of dye calculated as dye base in the standard powder, shows a 10% loss of dye by hydrolysis in the concentrated solution.

The upper limit of hydrolysis permitted under the definition of "storage stable" in this invention is 10% by weight of auramine base after storage in a tightly closed container for two months at 35° C.

The turbidity test is made by adding a sample of the concentrated solution of auramine base acetate to water to provide a 0.04% solution calculated as the dye base. A clear dilute aqueous solution shows that the dye has not hydrolyzed to the ketone.

Without limiting this invention, the following representative examples are given to illustrate our preferred mode of operation. Parts mentioned are by weight.

## EXAMPLE 1

*Part A.—Preparation of auramine base*

Crude auramine (dye hydrochloride, prepared according to the Feer process, method (1) on page 246 of Lubs, above cited), is extracted with cold water to remove most of the sodium chloride. One part of the dye thus obtained is dissolved in 20 parts of water at 60° to 65° C. The solution is clarified by filtration and cooled rapidly to 15° to 20° C. A 10% aqueous solution of sodium hydroxide is added to produce and maintain a positive test for alkali on phenolphthalein test paper, and agitation is continued at 15° to 20° C. until precipitation of auramine base is complete. This state is shown by a colorless or very light-colored ring when a test sample of the reaction mass is spotted on filter paper. The dye base is then filtered off, washed with cold water until free of alkali, and dried at a temperature not exceeding 60° C. until a test sample analyzes not more than 0.5% water.

All analyses for water content in this specification are meant to refer to water contents as determined by the Karl Fischer method (Anal. Chem., vol. 23, page 1069; 1951).

If desired, ammonium hydroxide, sodium carbonate, potassium carbonate or potassium hydroxide can be substituted for sodium hydroxide in the present example, the rest of the procedure being the same.

*Part B.—Preparation of the marketable composition*

Thirty-five parts of auramine base, prepared as in Part A, are stirred into 65 parts of glacial acetic acid having a water content of not more than 0.08%, while maintaining the solution temperature at 20° to 35° C. The solution thus obtained is clarified by filtration to remove insoluble material. Exposure to air is kept at a minimum so that the freshly prepared solution contains not more than 0.25% water.

The clear filtrate obtained is colored and constitutes a solution of auramine base acetate in acetic acid.

When the process of this example is repeated, except that 25 parts of auramine base and 75 parts of glacial acetic acid are employed, a storage stable concentrated dye solution is likewise obtained which gives satisfactory results in the turbidity and dyeing tests.

Similar results are obtained when 50 parts each of auramine base and glacial acetic acid are employed in Part B of this example.

For test purposes, the filtrate may be divided and stored in a series of closed containers for several months at temperatures ranging from 5° to 35° C. We have observed that all such stored samples remain fluid during the storage period, and that the samples stored even as high as 35° C. are stable against hydrolysis for at least two months. Thus, (1) dilution of the concentrated solution in water to form a 0.04% solution as dye base (i.e. 1.2 grams of the concentrated solution per liter of water), shows essentially no turbidity, and (2) a sample of the concentrated dye solution when subjected to comparative dyeing test against a sample of auramine standard dye powder (as indicated hereinabove) shows full dyeing strength.

If the procedure of Part B above is repeated except using acetic acid which contains 0.6% moisture (which rises to about 0.7% after the dye concentrate has been stored for two months at 20° to 35° C.), the dye solution still gives excellent results both by the turbidity test and by the comparative dyeing strength test above referred to.

When Part B is repeated except using 65 parts of propionic acid in lieu of the same quantity of acetic acid, the resultant concentrate analyzes 1.2% water after two months storage and when diluted as above to a dye concentration of 0.04% it exhibits appreciable turbidity.

Similar experiments have shown that when acetic acid is employed as solvent, the water content of the system generally rises with storage, but that as long as the final water content does not exceed 1.5%, its hydrolytic stability is not visibly affected. In other words, upon dilution with water to a dye concentration of about 0.04%, no more than slight turbidity is observed.

## EXAMPLE 2

*Mixture of acetic and hydroxyacetic acids*

Thirty-seven parts of auramine base, prepared as in Part A of Example 1, are stirred into a mixture of 57 parts of glacial acetic and six parts of hydroxyacetic acid while maintaining the solution temperature at 20° to 35° C. The dye solution is clarified by filtration.

In an actual experiment as in this example, analysis of the dye concentrate showed it to contain 0.74% moisture. Upon dilution with water, no turbidity was observed and the dye strength test showed the solution to be equal to the dye powder standard. When allowed to stand, however, for six weeks at 20° to 34° C., the moisture content of the solution rose to 1.8%, yet the solution, which showed considerable turbidity in the turbidity test, suffered only a 5% loss in tinctorial strength when tested by the dye strength method. In a similar experiment, when the moisture content of the concentrated dye solution was kept below 1.5% (same basis) during storage for six weeks, the product showed no loss in tinctorial strength when dyed on paper.

Similar results were obtained in experiments wherein the acid solvent component was made up of 44 parts acetic and 19 parts of hydroxyacetic acid; also, when the quantity of dye base added was varied from 25 to 50% of the weight of the whole.

## EXAMPLE 3

Auramine base, free of Michler's ketone and mineral acidity, and essentially free of water and water-soluble salts, is dissolved in glacial acetic acid at 25° C. in concentrations shown in the following table. The dye solutions are clarified by filtration and small amounts of water are added to portions of the samples A, C and E to provide the samples designated, respectively, as B, D and F. The samples are analyzed for water content and then are stored in tightly closed containers for two months at 20° to 30° C. The above described turbidity test is made at the completion of the storage period.

| Sample | Dye Base, Parts | Acetic Acid, Parts | Water Analysis, Percent | Turbidity |
|---|---|---|---|---|
| A | 10 | 90 | 0.4 | None. |
| B | 10 | 90 | 1.4 | Very slight. |
| C | 25 | 75 | 0.4 | Do. |
| D | 25 | 75 | 1.3 | Slight. |
| E | 35 | 65 | 0.4 | Do. |
| F | 35 | 65 | 1.3 | Slight to noticeable. |

All of the stored samples A to F show excellent dyeing strength on paper.

## EXAMPLE 4

*Dyeing procedure*

One part of the auramine base solution prepared in Part B of Example 1 is added to an aqueous slurry of 100 parts (dry basis) of bleached sulfite pulp in 5000 parts of water at room temperature. (This may vary in

normal plant practices from 2° C. in the winter in northern localities to 38° C. in the summer in warmer climates.) Two parts each of rosin size and aluminum sulfate octadecahydrate [$Al_2(SO_4)_3 \cdot 18H_2O$] are then added, the mixture is thoroughly agitated for 10 to 20 minutes and water is added to give a total of 20,000 parts. Paper sheet is then made up in the usual manner to provide yellow colored paper.

The amount of dye employed in this procedure may be varied from 0.05 to 1.0 part to give lightly tinted to deeply colored dyeings. The percent by weight of air dried paper pulp in the initial slurry may vary from 0.4 to 3. Likewise, the amount of rosin size and aluminum sulfate used may vary from about 0.5 to 3 parts and from 1 to 4 parts, respectively, or these additives may be omitted.

It will be understood that the details of the above examples may be varied within the skill of those engaged in this art. For instance, the concentration of the dye in the marketable solution is not critical, the lower limit being determined by economy and convenience in handling, while the upper limit (50%) is chosen to avoid unduly high viscosity in the solution. For optimum conditions, concentrations of 35 to 40% of dye base are recommended.

As already indicated, it is desirable to start with glacial acetic acid. Traces of moisture nevertheless enter the initial dye solution from the solvent, from the dye base and from the atmosphere. For improved stability, therefore, the acetic acid-dye solutions should be stored in tightly closed containers, and unused portions should be handled under conditions of minimum exposure to moisture.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A water-miscible, storage-stable, coloring composition of matter consisting essentially of a solution of auramine base in a solvent consisting of mixtures of acetic acid with hydroxyacetic acid containing the latter in a quantity not exceeding 30% by weight, said solution being essentially free of mineral acids, inorganic salts, salts of auramine base, and Michler's ketone, said solution being free of moisture in excess of 1.5% by weight and also free of acetic salts in excess of about 3% by weight.

2. A coloring composition as in claim 1, the quantity of auramine base therein constituting from 25 to 50% by weight of the entire composition.

3. A process for preparing a water-miscible, storage-stable, solution of auramine base, which comprises

(1) reacting auramine with a water-soluble alkali whereby to produce auramine base,

(2) filtering off the latter and drying the same at a temperature not exceeding 60° C. whereby to minimize hydrolysis of the base during said drying step, and

(3) dissolving the dried base at a temperature not exceeding 60° C. in a solvent consisting of mixtures of acetic acid with hydroxyacetic acid containing the latter in a quantity not exceeding 30% by weight, dissolving step excluding contamination of the solution with moisture in a quantity exceeding 1.5% by weight.

4. A process as in claim 3 wherein the auramine base filtered off in step (2) is washed with water at a temperature not exceeding 60° C. to remove excess alkali and by-product salts, prior to drying.

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