

1

2,727,062

STORAGE STABLE 4,6-DIAMINO METANILIC ACIDS

Vsevolod Tulagin, Binghamton, N. Y., assignor to General Aniline & Film Corporation, New York, N. Y., a corporation of Delaware

No Drawing. Application May 26, 1954,
Serial No. 432,601

5 Claims. (Cl. 260—509)

The present invention pertains to storage stable azine developers and more particularly to the stabilization of 4,6-diamino metanilic acid developers by crystallizing the same from an aqueous solution containing an alkali metal sulfite on the one hand and an alkali metal bisulfite on the other hand.

Schmidt and Tulagin, in their U. S. P. 2,486,440 granted November 1, 1949, and Gunther, in his U. S. P. 2,570,116 granted October 2, 1951, disclose that the development of light sensitive photographic material in color, wherein the color is imparted by an azine dye, is best effected by the utilization, as the color developer, of 2,4-diamino anilines. It is emphasized in both these patents that the most effective developers within this general category are those containing a sulfo group meta to the primary amino group, to wit, the metanilic acid derivatives.

The azine process as contemplated by the aforementioned patents has many attributes to recommend it. For example, the dye images obtained are much more stable, particularly to acid fumes than are the dye images obtained from quinoneimines and azomethines. However, the commercial exploitation and acceptance of this method have been, to a great extent, retarded by the fact that the 2,4-diamino anilines are very unstable products and deteriorate rapidly on storage.

It has been possible for several years to prepare the azine developers in a high state of purity. It has not been possible, however, to stabilize these developers or to preserve them during storage despite the great amount of work contributed to this problem. Thus, after as little as six months' storage in the dry state, the developers become a deep purple. A serious consequence of this transformation resides in the staining of the highlight or transparent portions of the azine film by the purple dyes so obtained. As a result, the azine materials display a pink toe or a pink highlight. The matter is further aggravated by the fact that the degradation of the developer is not of a limited nature but progresses indefinitely until the developer finally becomes completely useless even when carefully stored in the dried state.

It has been suggested that stability be imparted to the developers by the employment of known preservatives and, to this end, there have been used dextrose, hydroxylamine, p-hydroxyphenyl glycine and Rongalite, among others. It was found that even if some of these agents tended to effect stabilization, at the same time they injected some other problem which rendered their use intolerable. For example, dextrose, p-hydroxyphenyl glycine and Rongalite decrease the development potential. Hydroxylamine, conversely, causes a serious loss in color rendition by augmenting proximity development.

The particular problem involved was recognized and discussed in Gunther's U. S. P. 2,656,272 granted October 20, 1953. Gunther was aware of the ineffectiveness of preserving agents and sought to solve the difficulty by employing sodium metaborate as the sole alkali for the de-

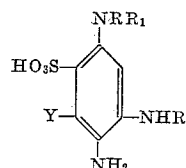
2

veloper. While the Gunther method permitted the realization of some stability, it was far from optimum and this is self-evident from a consideration of paragraph 1, column 6 of the patent.

Because of the seriousness of the developer instability and my recognition that the tactics previously followed had not yielded the result desired, I proposed to investigate the possibility of stabilizing the developer by chemically converting the same. I found that the 4,6-diamino metanilic acids readily formed crystals in aqueous solutions containing an alkali metal sulfite and an alkali bisulfite, and that surprisingly such crystals when in the dry condition were remarkably storage stable. Such crystals, for instance, could be stored for prolonged periods of time prior to use, and when incorporated in the developer solution reverted to the 4,6-diamino metanilic acid structure without loss of developing power.

4,6-diamino metanilic acids which are storage stable in the dry state and which are obtained by crystallization from an aqueous solution containing an alkali metal sulfite and an alkali metal bisulfite, and the use of the same as azine developers, constitute the purposes and objects of the present invention.

The 4,6-diamino metanilic acids contemplated herein are those described in the aforementioned U. S. Patents 2,486,440 and 2,570,116. These compounds may be typified by the following structural formula:



wherein R is hydrogen or alkyl, i. e., methyl, ethyl, propyl, butyl, amyl or the like and R₁ is an aliphatic radical such as alkyl as above, carboxy alkyl, such as carboxy methyl, carboxy ethyl, and the like; hydroxy alkyl, such as hydroxy ethyl, hydroxy propyl, and the like; aryl such as phenyl, toluyl and the like; carboxy alkyl aryl, such as carboxy methyl phenyl, carboxy ethyl phenyl, and the like, carboxy alkoxy aryl, such as carboxy methoxy phenyl, carboxy ethoxy phenyl; hydroxy alkyl aryl, such as hydroxy methyl phenyl, hydroxy ethyl phenyl, and the like; and hydroxy alkoxy aryl, such as hydroxy methoxy phenyl, hydroxy ethoxy phenyl and the like; R₂ is an alkyl group substituted by a hydrophilic group such as carboxy alkyl, such as carboxy methyl, carboxy ethyl and the like; hydroxy alkyl, such as hydroxy ethyl, hydroxy propyl and the like; sulfo alkyl such as sulfomethyl, sulfoethyl, sulfopropyl, sulfobutyl and the like, and Y is hydrogen, alkyl as above, sulfo or carboxy.

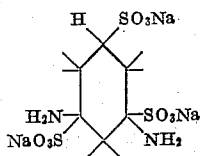
Examples of such developers are 2-phenylamino-4-(β-hydroxyethylamino)-6-phenylamino metanilic acid; 4,6-dimethylamino metanilic acid; 4,6-diphenylamino metanilic acid; 4,6-di(β-hydroxyethylamino)metanilic acid; 4-(β-hydroxyethylamino)-6-(4'-carboxymethoxyphenylamino)metanilic acid; 4-(o-methoxyphenylamino)-6-(p-methoxyphenylamino)metanilic acid and the like.

The storage stable crystalline products referred to above are readily made from the 4,6-diamino metanilic acids by dissolving the latter in a hot aqueous solution containing alkali metal sulfite on the one hand, such as potassium sulfite, sodium sulfite and the like, and an alkali metal bisulfite on the other hand, such as sodium metabisulfite, potassium metabisulfite and the like, cooling the solution and filtering the needle-like crystals which are formed. These crystals may be purified by washing with a solution of an alkali metal sulfite and bisulfite in water, followed by further washing with a low boiling organic solvent, such as isopropanol or mixtures thereof with methanol or

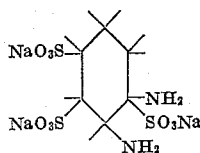
3

ethanol. The product is then dried, either in a stream of air or in vacuum. Preferably, to insure a good yield of such needle-like products, more than one mol of the bisulfite should be used per mol of the 4,6-diamino metanilic acid. Similarly, an excess of the alkali metal sulfite up to a saturated solution thereof is recommended for best results.

The particular structure of the storage stable crystalline products is not known, nor has the same been ascertained, although efforts to resolve the structure have been attempted. It has been found, as previously stated, that the storage stable products hereof precipitate as needles, whereas the 4,6-diamino metanilic acids are isolated in the form of plates. It is also known that the products hereof have extraordinary stability in the dry state as compared to the 4,6-diamino metanilic acids per se. It is my conviction, drawn from this phenomena, that the products are bisulfite addition products. It is to be pointed out, in this connection, that both 1,3-diamino benzene and 1,2-diamino benzene add three mols of sodium bisulfite to form non-aromatic addition complexes of the following constitution:



and



The azine developers, although they are triamines, possess both of the above structures and would, therefore, be expected to give non-aromatic alkali metal bisulfite addition complexes. The much higher resistance to oxidation exhibited by these addition complexes would then be completely explained by the fact that the aromatic structure has been destroyed. Thus, it is pertinent to observe that such compounds as ethylenediamine, ethanolamine and other purely aliphatic diamines and triamines are highly resistant to oxidation. It would, therefore, appear that the new compounds hereof are bisulfite addition products whose resistance to oxidation is traceable to the conversion of the aromatic form of the 4,6-diamino metanilic acids into an aliphatic form. However, analyses have not definitely established that such addition products are formed and, hence, I consider it preferable to characterize the products by their mode of formation.

The storage stable products are utilized in the formulation of photographic developers in the same manner as the 4,6-diamino metanilic acids per se. Thus, the developers may be made up in the same manner as disclosed in the aforementioned Patents 2,486,440; 2,570,116 and 2,656,272. Once such products are dissolved in water, particularly in the presence of an alkali, they revert to the 4,6-diamino metanilic acid structure and, as such, are effective in color development to produce azine dye images.

The following examples will serve to illustrate the invention, although it is to be understood that the invention is not restricted thereto. The parts are by weight unless otherwise stated.

Example I

2300 parts of water and 150 parts by volume of concentrated ammonium hydroxide are heated to 85°-95° C. in an open container equipped for agitation. 600 parts of sodium hydrosulfite are gradually introduced in small portions while insuring that each portion dissolves before

4

the next succeeding addition. When a solution has been obtained, 152 parts of the potassium salt of 2-phenylamino-4-(β -hydroxyethylamino)-5-nitrobenzenesulfonic acid are cautiously introduced in small portions. Concentrated ammonium hydroxide is also added at intervals to maintain the pH of the solution between 7 and 8. When reduction is complete, acetic acid is added to reduce the pH to from 5 to 6. (Acetic acid should be added until the solution assumes a distinct amber or brown color.) The reaction mixture is now decolorized, filtered and the filtrate treated with concentrated hydrochloric acid to effect crystallization of the product. The suspension is cooled and filtered and the collected solid thoroughly washed with a cold, concentrated solution of sulfur-dioxide in distilled water.

700 parts of hot water (distilled), 100 parts of sodium sulfite (anhydrous) and 50 parts of sodium metabisulfite are run into a container and the solution heated to boiling. The cake obtained by the previous reduction of the 2-phenylamino-4-(β -hydroxyethylamino)-5-nitrobenzenesulfonic acid is now introduced. (This cake is pale yellow in color and not pink.) After the components have dissolved, the boiling solution is treated with 150 parts of sodium metabisulfite. When a solution has been obtained, it is set aside to cool slowly without disturbance.

After 5 to 20 hours, the mixture is filtered. The collected crystalline solid is washed with several portions of a solution containing 100 parts of sodium metabisulfite and 50 parts of sodium sulfite in 350 parts of water. The solid is then washed with two portions of isopropanol and one of methanol and dried either in a stream of air in a vacuum.

The yield is approximately 83 parts of what appears to be the addition product of 4-(β -hydroxyethylamino)-6-phenylamino metanilic acid.

Example II

The procedure is the same as in Example I, excepting that there is used 150 parts of the potassium salt of 2,4-dimethylamino-5-nitrobenzenesulfonic acid in lieu of the potassium salt of 2-phenylamino-4-(β -hydroxyethylamino)-5-nitrobenzenesulfonic acid.

Example III

30 parts of 4,6-diphenylamino metanilic acid (prepared according to the procedure of U. S. P. 2,486,440) were dissolved in a solution of 110 parts of sodium sulfite and 80 parts of sodium metabisulfite in 700 parts of hot water. The resulting solution was allowed to cool slowly.

The crystalline solid was collected by filtration and thoroughly washed with a cold solution of 50 parts of sodium metabisulfite in 350 parts of water. It was then further washed with isopropanol and dried.

The white crystalline product thus obtained is the bisulfite addition product of 4,6-diphenylamino metanilic acid and is extremely stable to oxidation under normal storage conditions.

Example IV

The procedure is the same as in Example II, excepting that there is used an equivalent amount of 4,6-di(β -hydroxyethylamino)metanilic acid.

Example V

A photographic silver halide emulsion is exposed and developed in a black and white developer. The residual silver halide is re-exposed and developed in a developer of the following composition:

Sodium carbonate (monohydrate).....	parts.....	60
Potassium bromide.....	do.....	2
Sodium sulfite.....	do.....	40
6-N-ammonium hydroxide.....	parts by volume.....	20
Storage stable product produced as in Example I.....	parts.....	4
8-benzsulfonylamino naphthol.....	do.....	5
Water to make 1000 parts.		

5

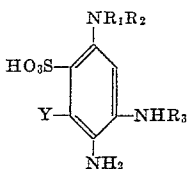
The film after development is bleached with a ferricyanide bleach and fixed in an acid hardening fixer. A positive azine dye image completely free from stain is thus obtained.

Various modifications of the invention will occur to operators in this field. Thus, it is self-evident that the procedure outlined above may be utilized for the stabilization of any of the 4,6-diamino metanilic acids described in U. S. Patents 2,486,440 and 2,570,116. I, therefore, do not intend to be limited in the patent granted except as necessitated by the appended claims.

I claim:

1. The storage stable products which result from crystallizing a 4,6-diamino metanilic acid from an aqueous solution containing an alkali metal sulfite and an alkali metal bisulfite.

2. The storage stable products which result from crystallizing, from an aqueous solution containing an alkali metal sulfite and an alkali metal bisulfite, compounds of the following formula:



wherein R₁ is selected from the class consisting of hydrogen and aliphatic radicals, R₂ is selected from the class

6

consisting of hydrogen, alkyl and aromatic radicals, R₃ is selected from the class consisting of aromatic radicals, a ring carbon atom of which is directly linked to the nitrogen atom and aliphatic radicals, a carbon atom of which is directly linked to the nitrogen atom, said carbon atom being substituted by at least two hydrogen atoms, and Y is selected from the class consisting of hydrogen, sulfo and carboxy.

3. The storage stable product which results from the crystallization of 4-(β-hydroxyethylamino)-6-phenylamino metanilic acid from an aqueous solution containing sodium sulfite and sodium bisulfite.

4. The storage stable compound which results from the crystallization of 4,6-dimethylamino metanilic acid from an aqueous solution containing sodium sulfite and sodium bisulfite.

5. The storage stable compound which results from crystallizing 4,6-diphenylamino metanilic acid from an aqueous solution containing sodium sulfite and sodium bisulfite.

References Cited in the file of this patent

UNITED STATES PATENTS

25	1,938,022	Huismann	Dec. 5, 1933
	2,592,363	Weissberger	Apr. 8, 1952
	2,603,657	Vinton	July 15, 1952
	2,611,785	Gunther	Sept. 23, 1952
	2,656,272	Gunther	Oct. 20, 1953