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CONCENTRATED BROWN DYE SOLUTION

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This application is a continuation-in-part of my co-pending application, Serial No. 227,939, filed Oct. 2, 1962, now abandoned.

This invention relates to the provision of stable, concentrated dye solutions. More particularly, it relates to the provision of storage stable, highly concentrated solutions of Bismarck Brown R in a mixture of sulfamic acid and certain organic acids.

Bismarck Brown R is a known basic azo dye prepared by tetrazotizing 2,4-toluylenediamine and coupling the tetrazo with 2,4-toluylenediamine. The new Color Index lists it under number C.I. 21,010 as "Basic Brown 4."

Bismarck Brown R has long been used for coloring paper products. The dyestuff is added during a "wet" stage in the process, to be distributed through the fiber mass by means of the water carrier. Conventionally, dyes, including Bismarck Brown R, are supplied to the paper manufacturer as carefully standardized powders or crystals. Rigidly controlled processing and inspection, plus carefully selected shipping containers, safeguard the uniformity and solubility of these powders or crystals. To achieve the desired color, two important dye-handling operations remain to be done at the mill: weighing the dye, and completely dissolving it either before or during contact time with the fiber.

It is in this area that improvement is possible, and highly desirable since weighing powders or crystals, in addition to being a time consuming operation, inevitably, upon each transfer of the dye from shipping container to scale to paper pulp, produces some hazardous dusting. Moreover, use of a solid-state dyestuff requires the step of dissolving it, which, if not substantially accomplished, results in a dye-specked product of reduced quality.

Attempts to produce Bismarck Brown R in the form of non-caking, freely flowing particles have not been successful, primarily because of the economics involved. Nor has the approach of preparing and shipping the dyestuff as a concentrated solution been successful. Solutions of useful dye concentration are difficult to prepare, and when prepared, are not so unstable to shipping and storage conditions, as to not meet commercial standards.

It is an object of the present invention to meet and avoid the aforementioned difficulties accompanying the use of Bismarck Brown R. More particularly, it is an object of the present invention to provide an aqueous dye solution of Bismarck Brown R which is simple to handle on a commercial scale, is stable and, unlike powdered and crystalline forms, also eliminates dusting problems and possible specking in the dye paper product. Other objects will become apparent upon a reading of the following detailed description.

In accordance with the present invention, previous difficulties encountered in the use of Bismarck Brown R are

substantially avoided by provision of an aqueous solution of the dyestuff containing dissolved sulfamic acid and a 1–3 carbon alkanoic acid. Such solutions can be prepared in dye concentrations as high as about 35%. They are simply handled, pose no dusting problems, are volumetrically measured with ease, and give a dyed product free of undissolved dye specks.

Dye solutions of the present invention are prepared by dissolving Bismarck Brown R Base in water containing sulfamic acid and an alkanoic acid having from one to three carbon atoms (i.e., formic, acetic or propionic acids). Dissolution may be hastened by slight agitation either at room or slightly elevated temperature.

For good results, it is necessary to comply with certain proportional requirements. Solutions containing up to 35% dyestuff are obtainable and useful, but higher concentrations, though possible, are not desirable since such usage is accompanied by increased viscosity, restricting free-flow of the solution. Solutions having lower dye concentration, i.e., in the range of 10–30%, particularly, 15–25%, are preferred for ease of preparation and stability. Lower concentrations, i.e., from 1–10%, may be useful in some instances, but are normally not desired because of the increased shipping cost per unit of dye.

At least one weight percent of sulfamic acid for each part of aqueous solution should be used. Up to 35 percent may be employed. For greatest net effect, between 5 and 30%, particularly within the range of 10–20%, of the aqueous dye solution should be composed of sulfamic acid.

The range of alkanoic acid usage is about the same as sulfamic acid. The total amount of the former may be somewhat less than that of the latter and may be comprised of a mixture of two or more of formic, acetic and propionic acids. In general, it is preferred to have about 5–15% of the alkanoic acid in the final dye solution.

To prepare dye solutions of higher concentration, the sulfamic acid and alkanoic acid components should be employed in the higher sectors of the above-stated ranges. Solutions of lower dye concentrations require proportionately lower usage of the acid components.

The invention is illustrated by the following examples and tests results.

A series of aqueous Bismark Brown R dye solutions (Examples A–I) were prepared using the following acids:

(A) Sulfamic acid only;
(B) Formic acid only;
(C) Acetic acid only;
(D) Propionic acid only;
(E) Hydrochloric acid only;
(F) Sulfamic acid and formic acid;
(G) Sulfamic acid and acetic acid;
(H) Sulfamic acid and priopionic acid; and
(I) Sulfamic acid and hydrochloric acid.

All of these solutions were made by adding the solid dye to the water solution of the respective acid or acids with stirring and, when necessary, warming the solution to effect solution of the dye. Equivalent amounts of total acids were used throughout. The proportions of components in these solutions, on a parts by weight basis, are shown in Table I.

TABLE I

Solution	A	B	C	D	E	F	G	H	I
Bismarck Brown Base	25.0	25.0	25.0	24.0	25.0	25.0	25.0	25.0	25.0
Sulfamic Acid	28.4					15.5	15.5	15.5	15.5
Formic Acid		13.5				6.2			
Acetic Acid			17.6				8.0		
Propionic Acid				21.7				9.9	
Hydrochloric Acid (20° Bé.)					34.0				15.4
Water	46.6	61.5	57.4	54.3	41.0	53.3	51.5	49.6	44.1
Totals	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

It was found that two of these solutions, i.e., Solution E, prepared from hydrochloric acid alone, and Solution I, prepared using sulfamic acid and hydrochloric acid, formed a solid precipitate, which appeared to be crystals of the dye salt, on standing for only a few minutes. Also, Solution D, prepared from proprionic acid only, began to develop an insoluble material after standing for several days. This material, believed to be a decomposition product of the dye, continued to form and settle out of the solution on further standing.

Samples of the other solutions, A–C and F–H, which did not develop solid matter but which exhibited an increase in viscosity on standing, were subjected to storage tests as follows. Each sample was analysed spectrophotometrically for strength and (except in the case of Solution H) the viscosity thereof determined (a) on the day of preparation (b) after 1 week and (c) after 1 month of storage at room temperature. The results of these tests are given in Table II. No viscosity measurements were made on Solution H, since it was very fluid when prepared and remained so over the entire storage period.

TABLE II

Solution	A	B	C	F	G	H
Initial:						
Strength, percent [1]	52	48	50	47	49.5	52.8
Viscosity, cps. (21° C.)	2,350	1,010	580	1,265	750	
1 Week:						
Strength, percent [1]	52	46	49	47	50.1	
Viscosity, cps. (21° C.)	12,410	8,040	9,110	2,000	3,820	
1 Month:						
Strength, percent [1]	51.9	44	44.9	46.7	50	50.8
Viscosity, cps. (21° C.)	16,100	12,100	9,600	2,400	4,400	

[1] Relative to a commercial dye as standard.

It will be seen from Table II that Solutions A–C, prepared using only a single acid, i.e., sulfamic acid, formic acid and acetic acid, respectively, exhibited marked increases in viscosity on standing and that Solutions B and C decreased significantly in strength.

On the other hand, Solutions F and G prepared using sulfamic acid in combination with formic and acetic acids, respectively showed good strength retention and only relatively low viscosity increases. The solutions and Solution H are, therefore, entirely satisfactory for use as dye solutions, whereas Solutions A–C are not. Also, Solutions D, E and I, which developed insolubles as previously described, are obviously not suitable for this use.

It will be appreciated further that the combination of sulfamic acid with higher carboxylic acids would have deficiencies which would make them unattractive even if they should form stable dye solutions. For example, the unpleasant odor associated with butyric acid would preclude its use on a commercial basis.

I claim:

1. An aqueous dye solution comprising on a weight basis (a) 10–30% of C.I. 21,010, (b) 10–20% of sulfamic acid, and (c) 5–15% of an alkanoic acid of 1–3 carbon atoms.

2. The solution of claim 1 wherein the alkanoic acid is formic acid.

3. The solution of claim 1 wherein the alkanoic acid is acetic acid.

4. The solution of claim 1 wherein the alkanoic acid is propionic acid.

5. The solution of claim 1 wherein the alkanoic acid is a mixture of 1–3 carbon atom alkanoic acids.

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