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VAT DYEING OR DYE STRIPPING WITH ALKALINE BOROHYDRIDE AND HYDROSULFITE SOLUTION

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The present invention relates to a new and improved method for conducting chemical reductions, and particularly chemical reductions wherein hydrosulfite is the principal reducing agent as in vat dyeing; and the invention also relates to novel compositions comprising hydrosulfite and alkali metal borohydrides for use according to the new method. This application is a continuation-in-part of application Serial No. 96,115, filed March 16, 1961, now abandoned.

Chemical reduction of materials using hydrosulfite as the reducing agent is well known. Equally well known, particularly in reducing operations on a commercial scale wherein the reducing medium is subjected to air, agitation and high temperatures, is the instability of the hydrosulfite resulting in large losses of hydrosulfite through air oxidation and the often undesirable measures required to reduce or compensate for this loss.

Vat dyes are characterized by their ability to be reduced to a leuco form and then be oxidized back to their original form. In accordance with one technique of vat dyeing, the textile to be dyed is passed through a dye bath or otherwise contacted with the dye, in vat dye pigment form, and then the dye carrying textile is passed through a hydrosulfite vat dye reducing medium. The reducing medium serves to reduce the dye to its leuco form thereby enabling the dye to thoroughly penetrate and saturate the fiber. The textile impregnated with the reduced vat dye then is subjected to an oxidizing operation to oxidize the dye back to its original form. The reducing medium employed prior to the present invention usually has been an aqueous solution of an alkali metal hydrosulfite, such as sodium hydrosulfite. Since alkali metal hydrosulfites decompose very rapidly in aqueous solution under the conditions of air oxidation encountered in dyeing in commercial equipment, particularly in continuous dyeing operations where high temperatures are used and where the material being dyed contains much entrained air which is agitated into the reducing solution, the reducing solution contained a large amount of caustic alkali to render the alkali metal hydrosulfite sufficiently stable for the contemplated use, and large amounts of hydrosulfite had to be added from time to time to compensate for that consumed by air oxidation.

Alkali metal borohydrides are known reducing agents; however, such compounds are quite expensive in cost, thus prohibiting their use, particularly in the textile field, except in the case where very minor amounts would be of material benefit. The preferred use of the alkali metal borohydrides from a standpoint of economy and ease of operation is in the form of an aqueous solution. However, alkali metal borohydrides when placed in an aqueous solution possess an inherent instability due to the fact that when dissolved in water, the compound immediately begins to decompose rather rapidly into an alkali metal metaborate with an evolution of hydrogen. It has been found that a stabilized aqueous solution of the alkali metal borohydrides can be produced by the addition of sodium hydroxide or like caustics to the alkali metal borohydride solution, thereby elevating the pH above the normal pH of 9.5 possessed by the solution. Thus today a stable aqueous solution of an alkali metal borohydride

on a strongly alkaline side is readily available. However, the alkali metal borohydrides in a strongly alkaline solution, when used alone, have been found not to be generally satisfactory in the textile field where a high reducing activity is required, since the higher the alkalinity the less reactive the borohydrides become.

The use of a borohydride to reduce a bisulfite to a hydrosulfite, which may then be used to reduce vat dyes, has been suggested. However, this offers no significant advantage in the textile field. In one procedure involving this suggestion, the vat dye, bisulfite and borohydride are combined with the resultant reduction of the dye. Caustic soda is then added and the solution used as a dye. The only advantage alleged for this procedure is the more rapid reduction of the dye as compared to the use of hydrosulfite alone.

Some attempts have been made prior to the present invention to achieve an acid leuco dye. In these attempts, the vat dye was reduced to the alkali leuco form by a conventional alkali metal hydrosulfite alkali metal hydroxide reducing solution and this was then neutralized by the addition of acetic acid or the like and employed in this form. This operation of acid neutralization of the conventional reducing solution to produce an acid leuco vat dye is, in effect, a titration on a large scale which is not commercially practical for dyeing as distinguished from padding or impregnating. The only utilization of such acid vat dyeing heretofore has been to provide an initial penetration of high twist yarn cellulose fabrics to dye them in light shades or to overcome specking in light shades, such paddings or impregnations being dyed subsequently to the desired shade by contacting the textile in a fresh reducing solution containing an alkali metal hydrosulfite and an alkali metal hydroxide to convert the dyestuff to the conventional alkali leuco form.

It has been found in accordance with the present invention that alkali metal borohydrides may be combined with a hydrosulfite vat dye reducing medium to produce compositions that give new and novel results and which are commercially feasible to employ. More particularly, it has been found in accordance with the present invention that alkali metal borohydrides when combined with a hydrosulfite produce a completely stable composition having a truly synergistic effect when employed as a reducing agent in reducing operations under conditions at which, but for the presence of the borohydride, a large proportion of the hydrosulfite would be lost due to air oxidation.

The present invention is based in part upon the discovery that in reducing a vat dye a large portion of the amount of hydrosulfite normally required for providing and maintaining reducing conditions, particularly in continuous dyeing procedures, can be eliminated by employing, in conjunction with the hydrosulfite, an alkali metal borohydride, such as sodium borohydride. Hence, the invention will be described with particular reference to reduction of vat dyes; however, it will be apparent from the following description that the invention is broader in scope.

While it can be shown that (theoretically) one part by weight of sodium borohydride is the equivalent of 18.5 parts by weight of sodium hydrosulfite as a reducing agent, I have discovered that one part by weight of borohydride can eliminate up to several hundred or more parts by weight of hydrosulfite when the borohydride and hydrosulfite are used in conjunction for reducing vat dyes. The greatest savings in hydrosulfite consumption will be realized, of course, in continuous dyeing procedures where the reducing solution is subjected to severe air oxidation conditions and where, according to my invention, hydrosulfite need be supplied to the system only in an amount

approximating that removed as such physically from the system by passage of the material being dyed therethrough (entrainment on the material, overflow to compensate for liquid contained in the incoming material, and leakage) as contrasted to the large amounts in excess of this conventionally required to compensate for hydrosulfite lost through air oxidation.

In my process it is believed that the hydrosulfite is still the reducing agent for the dye. Thus, it is believed, the borohydride serves primarily to stabilize the hydrosulfite against air oxidation. At any rate there is a marked synergistic action exerted by the combination, particularly under conditions of air oxidation encountered in commercial operations, which cannot be obtained by either component alone and which are not realized under most small scale operations where air oxidation is negligible.

It has been further found in accordance with the present invention that hydrosulfite when combined with an alkali metal borohydride at a pH in the neighborhood of 10 (without the use of an alkali metal hydroxide) provides an acid leuco vat dye directly usable as such.

It is therefore a principal object of the present invention to provide a new and improved method for conducting chemical reductions.

Another object of the invention is to provide a new and improved method for reducing materials with hydrosulfite wherein substantial savings in hydrosulfite consumption are afforded.

Still another object of the invention is to provide a new and improved method of dyeing fibers, yarns, fabrics and the like.

A further object is to provide a new and improved method of vat dyeing wherein substantial savings in hydrosulfite consumption are afforded.

A still further object of the invention is to provide an improved method for treating cellulosic textile fabrics to reduce or prevent fiber degradation.

A further object of the present invention is the provision of a new and improved method of dyeing wherein the hydrosulfite vat dye reducing composition is quite stable under all conditions and possesses a prolonged reducing life for vat dyes.

Still another object of the present invention is the provision of a new and improved method of dyeing giving a more effective and uniform dyeing than heretofore possible.

A further object of the present invention is the provision of a new and improved method of vat dyeing wherein excellent dyeing is achieved at high temperatures.

Still another object of the present invention is the provision of a new and improved method of vat dyeing which does not require the amounts of certain compounds therein which might be harmful to certain materials if present in large amounts.

A further object of the invention will be to provide method and results for the stripping of vat and azoic dye colors from textile fibers and fabrics.

Yet another object of the present invention is the provision of a new and improved method of vat dyeing that may be employed efficiently and effectively on articles heretofore found unsuitable for dyeing in a vat dye operation.

It is another principal object of the present invention to provide a new and novel composition containing hydrosulfite and an alkali metal borohydride.

Further and additional objects will become manifest from the ensuing description.

It has been found in accordance with the present invention that a new and novel reducing composition for effectively reducing vat dyes in a new and improved manner is possible with the combination of a hydrosulfite and an alkali metal borohydride. Such a reducing composition is equally effective as a reducing agent either in the presence of an added alkali metal hydroxide, such as, for example, sodium hydroxide, or in the absence of any added alkali metal hydroxide to produce the acid leuco form of the dye. Such a reducing composition makes it possible to materially reduce the amount of alkali hydrosulfite or caustic heretofore found necessary and yet achieve a very effective dyeing of the textiles.

In a preferred embodiment, the material to be dyed is first contacted with the vat dye pigment and is thereafter contacted with the hydrosulfite vat dye reducing medium containing the alkali metal borohydride. This can be either a continuous or a batch operation. In continuous operation, the material is passed into contact with a dispersion of vat dye pigment, and thereafter passed into contact with the hydrosulfite vat dye reducing medium. The passage of the material through the air and into and through the reducing medium introduces much air into the latter which is mixed into the reducing medium by virtue of the motion involved. In accordance with the present invention however, this does not significantly affect the hydrosulfite which is stabilized by the borohydride. In batch operation, the material to be dyed, usually wet with scouring and rinse liquor, is contacted with a dispersion of vat dye pigment. The material is then contacted with the hydrosulfite vat dye reducing medium, as by placing the material in the reducing medium or by adding the reducing medium to the material.

In another embodiment, the dye is first reduced to the acid leuco form with the hydrosulfite and borohydride, and the material to be dyed is contacted with the resulting dye. This procedure provides a means for carrying out vat acid dyeing which possesses many obvious advantages over the conventional procedure as referred to hereinabove, and can be used in either continuous or batch operations. In this case the material may subsequently be contacted with an alkali metal hydroxide (with or without the presence of further hydrosulfite and borohydride) to convert the dye to the alkali leuco form.

In still another embodiment the vat dye is reduced by the hydrosulfite to the alkali leuco form in the presence of the borohydride and an alkali metal hydroxide at a pH above 10, and the material is contacted with the dye in the alkali leuco form.

In vat dyeing operations there is an exhausting phase during which the dye in leuco form migrates from the dyeing medium into the material being dyed. As is well known each vat dye has its own temperature of maximum exhausting rate. However, it is preferred to exhaust at a temperature above this in order to achieve better control over the exhaust rate and hence better levelling and quality of dyeing. One of the principal advantageous features of the present invention is the ability provided to allow a more controlled exhaust at high temperatures, that is above about 160° F. The preferred exhausting temperature in accordance with the present invention (balancing all factors involved in determining a dyeing procedure), particularly with continuous operation, is in the neighborhood of 190–205° F. Exhausting can take place in the reduced dye bath or in the reducing medium by maintaining these at the desired temperature, or exhausting can take place beyond these media in a separated heating step, such as in steam, molten metal, hot oil, and the like. The upper temperature limit will be dictated largely by the nature of the material being dyed as well as the heating techniques available. In some cases the temperature may run as high as 500° F.

In accordance with the present invention, the alkali metal borohydride employed may be sodium borohydride, potassium borohydride, lithium borohydride, and the like. Of the foregoing, the preferred compound is sodium borohydride. The alkali metal borohydride may be employed in solid form or may be employed in the form of a stabilized aqueous solution.

The hydrosulfite serving as the vat dye reducing agent in the vat dye reducing medium may be any alkali metal hydrosulfite such as, for example, sodium hydrosulfite, lithium hydrosulfite, potassium hydrosulfite, or the like.

It may also be ammonium hydrosulfite as referred to below. The hydrosulfite may be used as such or may be formed in situ in the reducing medium through the use of another sulfur compound, like an alkali metal bisulfite or sulfurous acid, reducible by the borohydride to the corresponding hydrosulfite. When sulfurous acid is used as the source, ammonium hydroxide will normally also be employed to provide ammonium hydrosulfite in the solution. When the hydrosulfite is formed in situ by reduction, sufficient excess borohydride will be employed to insure an amount remaining in the reducing medium as hereinafter set forth. It is preferred to employ a hydrosulfite as such.

In the practice of this invention care must be exercised in the amount of alkali material, such as sodium hydroxide, employed in the reducing medium since the presence of the alkaline material in excessive amount has a tendency to suppress the activity of the alkali metal borohydride so that it in turn cannot stabilize the hydrosulfite. In the practice of the invention the reducing medium will have a pH between about 9.5 and about 13. A pH in the lower portion of this range, i.e. below about 11, can be provided by using ammonium hydroxide without using any alkali metal hydroxide. In the practice of this aspect of the invention if ammonium hydroxide is used as the alkaline material, it is possible effectively to dye textile material, which would be subject to degradation in the presence of alkali metal hydroxide, without fear of alkali metal hydroxide degradation regardless of the temperatures encountered or the time of contact of the textile with the reducing medium. A pH in the upper portion of this range, i.e. above about 11, is suitable for the dye in alkali leuco form. This pH can be provided by using an alkali metal hydroxide.

The hydrosulfite vat dye reducing medium in accordance with the present invention will contain, in addition to hydrosulfite, an alkali metal borohydride, in an amount of at least about 0.0005%, by weight, of the medium. Generally, amounts in excess of 2% are unnecessary and represent a waste of materials. In continuous dyeing operations the borohydride is present in a preferred amount from 0.01% to 0.1%. In package dyeing operations, however, the borohydride is present in a preferred amount from 0.005% to 0.05%. Hydrosulfite will be present in an amount of at least about 0.025% and may go up to about 2%, or even higher although greater amounts are usually unnecessary and represent waste. Preferably in continuous dyeing operations, hydrosulfite is present in an amount between about 0.1% and about 1%, whereas in package dyeing hydrosulfite is present in an amount between about 0.05% and about 0.5%. It will be obvious to one skilled in the art that the above noted variations in preferred quantities of components in the reducing media are the result of variations in apparatus, techniques, and liquor/textile ratios as well as the quantity of dye necessary to be reduced. It will be further obvious that variations from these preferred amounts but still within the broad range will be necessary as equipment, technique, quantity of dye, and liquor/textile ratio are varied.

The hydrosulfite vat dye reducing medium employed in accordance with the present invention will most often be in the form of a solution. The preferred carrier from a standpoint of economy and ease of use is, of course, water, so that aqueous solutions are preferred. However, it is to be clearly understood that any other liquid vehicle in which the ingredients are soluble or dispersible and which will be non-reactive (inert) with the ingredients, or will in no other way deleteriously affect the dyeing operation, may be used. Likewise the vat pigment will most often be employed as a dispersion in water, although it will be understood that any other liquid vehicle in which the vat pigment can be dispersed or dissolved, and which will not deleteriously affect the dyeing operation, may be used.

The concentrations set forth herein are based on a ratio of liquid reducing medium to material being dyed of at least 0.5:1 (weight basis) which means that if the ratio is less than 0.5:1, the concentrations might have to be increased accordingly.

One of the important features of this invention is the improved control of exhaust rate due to the lower overall concentration of the electrolyte material required for reduction. Where the conventional caustic hydrosulfite reduction medium may have a required electrolyte concentration of such degree that retardants are necessarily employed to depress the rate of dyeing, such components are generally not necessary in the practice of the present invention. However, it will be understood that the reducing medium used may contain electrolytes, such as sodium chloride, sodium sulfite, sodium sulfate, potassium chloride, potassium sulfate, and the like, to enhance the reducing activity by increasing the ionic strength and to increase the rate of exhaustion of the reduced dye.

It is surprising that the alkali metal borohydride and hydrosulfite may be used in combination in an aqueous solution without added alkali metal hydroxide (although ammonium hydroxide can be used) in view of the fact that either of these components when used alone in an aqueous solution tend to decompose at a fairly rapid rate.

I am able to utilize the aforementioned reduction in the lower portion of the stated pH range to produce a vat acid leuco dye which is sufficiently stable at the temperatures encountered in the dyeing operation for a period of time sufficient to satisfactorily dye textile articles on a large scale commercial basis. Vat acid leuco dyes have not been employed commercial heretofore in a dyeing process in which there is no subsequent conversion to the alkaline leuco. The present invention enables the textile dyer to prepare a commercially stable acid leuco vat dye that can be utilized for dyeing without further conversion under conditions of both high temperature and agitation. Heretofore, when vat acid leuco dyeing had been employed, large, excessive amounts of alkali metal hydrosulfite were required to maintain the acid leuco vat dye form under the conditions of air oxidation encountered in dyeing on or in commercial equipment, since the hydrosulfite decomposes very rapidly unless a considerable amount of an alkali metal hydroxide or other alkaline material is added, and the temperature had to be kept depressed. It should be understood that, in this embodiment, reference is made to "acid" leuco vat dye since of the three conventional forms (pigment or oxidized, acid leuco and alkali leuco) known in the dyeing art, this embodiment most closely resembles the acid leuco form; however, qualitatively, the dye may be in predominantly acid form, predominantly ammonium salt form, or in a mixed form.

The acid leuco vat dyes formed in accordance with the present invention are commercially practical and useful in virtually all forms of vat dyeing. Moreover, the acid leuco vat dyes formed in accordance with the present invention are in a more finely dispersed form than those provided by the above-mentioned "titration" method of forming acid vat leuco dyes, which enhances the impregnating and dyeing characteristics. The attainment in accordance with the present invention of a stable vat acid leuco dye makes it possible to dye synthetic yarns and fabrics, such as, acetate and triacetate, nylon, acrylic, and polyester, etc.; and naturally occurring animal fibers, such as, for example, wool and silk. However, the acid leuco vat dyes of the present invention possess little or no affinity for unmodified or regenerated cellulosic fibers or fabric, and as a result, it is possible to achieve a selective dyeing of synthetic fibers or yarns blended with cellulosic fibers or yarns. The selective dyeing of a synthetic yarn in the presence of cellulose or alternatively another synthetic yarn may be enhanced by the addition of other compounds to the system; for example, an addition of

benzyl alcohol to the reducing system will cause the vat acid leuco to dye nylon in preference to anything else. Alternatively, the addition of aniline or methyl salicylate to the vat acid leuco system will cause polyester to be preferentially dyed. Another example: the addition of cupric sulfate to the vat acid system will cause an acrylic fiber to be preferentially dyed. Thus it is possible in accordance with the present invention to dye textiles containing synthetic and cellulosic fiber blends without materially dyeing the cellulose. Furthermore, by adjusting the pH by the addition of an alkaline material to form the alkaline or conventional leuco form of the vat dye, the cellulose can be dyed as a second step in the same reducing bath with the same color.

Another advantage attainable with the acid leuco dyes of the present invention is that it makes it possible to dye most or all textile materials with little or no harmful results. In dyeing silk, wool, and like textile materials with conventional caustic vat dye leucos heretofore, there is always a likelihood of fiber degradation due to the presence of the alkali metal hydroxide in the reducing solution. As a result, dyeing of such materials with vat dyes has been possible without damage only at low temperatures and a short contact period of the fabric with the reducing solution. Such requirements have obviously limited the dyeing of such textiles on a large scale basis with vat dyes. However, with the acid leuco vat dyes of the present invention, since no alkali metal hydroxide is present, it is possible to dye textile material that may otherwise be subject to degradation by the presence of alkali metal hydroxide in the reducing solution with vat dyes.

Additionally, cellulosic textiles dyed with an alkali metal vat leuco according to the invention suffer little or no degradation from the presence of an alkali metal hydroxide due to the protective action of the reducing medium; i.e., alkaline oxidation of hydroxyl groups on the cellulose is immediately counteracted by reduction back to the hydroxyl stage.

Instances occur in commercial vat dyeing, since it involves human judgment, where the dyeing is not acceptable as to shade even though the dyeing may be standard in all other respects. As a consequence a portion of the dye must be removed from the substrate sufficient to allow the yarn or fabric to be redyed to the acceptable shade. This is conventionally accomplished by immersing the dyed substrate in a caustic-hydrosulfite reduction bath which reduces the vat dye on and within the substrate to the soluble sodium leuco form with a subsequent equilibrium shift of a portion of the reduced color from the substrate to the bath. This equilibrium shift is conventionally enhanced by the addition to the reducing bath of additives such as polyvinyl pyrrolidone, sodium lignin sulphonate, etc. Additionally if the amount of dye to be removed is extensive, the dye substrate may require subjection to the reducign bath more than once. Since each exposure to the reducing bath is detrimental by reason of alkaline oxidation and costly with respect to the amounts of chemicals required, the time lost, and the labor, power, etc. costs involved, it is obvious that the invention practice, by virtue of its ease in shifting the reduced dye equilibrium further in the direction of the bath as well as its minimizing of alkaline oxidative degradation and its ability to be similarly enhanced by the addition of any conventionally used additive, facilitates the removal of vat dyes from a dyed substrate with greater ease and safety than heretofore possible. Hence the hydrosulfite vat dye reducing medium, containing the alkali metal borohydride, as described herein may be used to remove vat dyes from vat dyed material. As will appear, the procedure may also be used to remove dyes containing azoic linkages from materials dyed therewith.

It should be noted that the practice of the color stripping invention on substrates dyed with both vat dyes and dyes containing azoic linkages facilitates the color stripping of rags with greater ease and safety than heretofore possible.

The following example is illustrative of the above stripping procedure.

EXAMPLE I

A reducing bath was made according to the following proportions:

	Lbs.
Sodium borohydride	0.1
Sodium hydrosulphite	1.0
Sodium hydroxide	6.0
Water to make 85 gallons.	

This bath was maintained at a temperature of 200° F.±3° F. and constantly replenished from an identically formulated reserve, held at a temperature of 100° F. as needed. Dry cotton fabric previously dyed a medium green shade with Vat Green #1, C.I. 59875 was passed continuously through this reducing bath at a speed such that the immersion time was 10 seconds, rinsed with cold water, oxidized with sodium perborate and acetic acid, soaped at 200° F. in the presence of a nonyl phenyl ethylene oxide condensate and soda ash, rinsed and dried. The dyed shade showed a marked loss in tinctorial strength as compared to the original dyed sample and was appreciably lighter in shade than a portion of the originally dyed sample passed through a conventional caustic-hydrosulfite vat color stripping bath of formulation

	Lbs.
Sodium hydrosulfite	24
Sodium hydroxide	24
Water to make 85 gallons.	

held at the same 200° F.±3° F. as above described and constantly replenished from a reserve as needed to maintain the bath volume and reducing capacity.

The method of the present invention is of particular utility in the dyeing of textile fabrics with vat dyes either in the alkaline leuco form or the acid leuco form. In utilizing the present invention in the vat dyeing of textiles, I believe any vat dye may be employed. Illustrative examples of such vat dyes that may be employed are the anthraquinone type dyes containing no amino groups, such as, for example, Indanthrene Golden Yellow RK (Vat Orange 1, C.I. #59105/6), Indanthrene Brilliant Orange RK (Vat Orange 3, C.I. #59300), Amanthrene Golden Orange F (Vat Orange 9, C.I. #59700), Indanthrene Orange RRT (Vat Orange 1, C.I. #59705), and Indanthrene Dark Blue BO (Vat Blue 20, C.I. #59800), Tinon Navy Blue RAF (Vat Blue 18, C.I. #59815), Ahcovat Jade Green B (Vat Green 1, C.I. #59825), Indanthrene Brilliant Violet 3B (Vat Violet 9, C.I. #60005), Cibanone Violet 4R (Vat Violet 1, C.I. #60010); anthraquinone type dyes containing amino groups, such as, for example, Cibanone Black DRB (Vat Black 9, C.I. #65230); dyes containing a heterocyclic nucleus fixed to a central vatting system, such as, for example, Indanthrene Red FBB (Vat Red 10, C.I. #67000), Tinon Yellow GC (Vat Yellow 2, C.I. #67300), Carbanthrene Red BN (Vat Red 35, C.I. #68000), Cibanone Violet BNA (Vat Violet 13, C.I. #68700), Indanthrene Brown RN (Vat Brown 3, C.I. #69015), Indanthrene Red Brown 5RF (Vat Brown 25, C.I. #69020), Tinon Olive BF (Vat Green 3, C.I. #69500), Tinon Olive SF (Vat Black 25, C.I. #69525), Cibanone Blue GCDN (Vat Blue 14, C.I. #69810), Ponsol Blue BF (Vat Blue 6, C.I. #69825), Indanthrene Khaki GG (Vat Green 8, C.I. #71050); indigo and its derivatives and homologues, such as, for example, Cibanone Blue 2BGD (Vat Blue 5, C.I. #73065); thioindigo and its derivatives and homologues, such as, for example, Hostavat Brilliant Pink R (Vat Red 1, C.I. #73360), Indanthrene Printing Violet 6R (Vat Violet 3, C.I. #73395); phthalocyanine dyes,

such as, for example, Algol Brilliant Blue 4G (Vat Blue 29, C.I. #74140).

In the comparative commercial runs given in each of the following tables, the same procedure was followed. The fabric to be dyed was immersed in an aqueous dilution of the vat dyes as purchased commercially, squeezed to a constant pick up of about 70%, air dried, then passed through a Williams unit containing the reduction bath. The immersion period in the Williams unit ranged from 7 to 10 seconds with the immersion periods of comparative runs being identical. The fabric was in all cases then removed from the reduction bath, rinsed with cold water, oxidized with sodium perborate and acetic acid, soaped at 200° F. with a commercially available nonyl phenyl ethylene oxide condensate and soda ash, rinsed with hot water, then cold water and dried. In all cases the desired dye shade resulted, and in each case the amounts given are for treatment of the same amount of material as designated in each table.

The figures for the reducing bath given in each column A represent the amounts of chemicals used to set the Williams unit initially to the required reduction potential plus the amounts added during the operation such that the volume of the reducing bath was maintained throughout the passage of the designated amount of fabric therethrough. These amounts added also maintained the initial reduction potential of the bath. On the other hand, the figures for the reducing bath in each column B represent the amounts of chemicals used to set the Williams unit initially to the required reduction potential plus the amounts added during the operation to maintain the initial reduction potential of the bath throughout the passage of the fabric therethrough. In this case the replacement feed is substantially more concentrated in order to compensate for air oxidation.

Table 1

[Shade: Sand. Goods: Cotton (8,380 yds.)]

Chemicals, etc.	A	B
	Pounds	*Pounds*
Indanthrene Brown Inf. Dbl. Pst. Vat Brown 5 C.I. #73410	16.55	16.55
Indanthrene Grey 2GF Inf. Dbl. Pst. Vat Black 20	2.145	2.145
Carbanthrene Brown BR Pst. Vat Brown 1 C.I. #70800	2.60	2.60
Indanthrene Brown RN Inf. Dbl. Pst. Vat Brown 3 C.I. #69015	.10	.10
Sodium borohydride	.98	
Sodium hydroxide	36.60	82.00
Sodium hydrosulfite	16.60	82.00
Sodium chloride	115.0	

Table 2

[Shade: Buttercup. Goods: Cotton (14,500 yds.)]

Chemicals, etc.	A	B
	Pounds	*Pounds*
Cibanone Yellow P2GA Dbl. Pst. Vat Yellow	5.86	5.86
Cibanone yellow GC Pst. Vat Yellow 2 C.I. #67300	7.00	7.00
Sodium borohydride	2.11	
Sodium hydroxide	37.50	64.00
Sodium hydrosulfite	10.65	64.00
Sodium chloride	41.00	

Table 3

[Shade: Pink. Goods: Cotton (5,300 yds.)]

Chemicals, etc.	A	B
	Pounds	*Pounds*
Carbanthrene Red FBB Dbl. Pst. Vat Red 10 C. I. #67000	4.30	4.30
Brilliant Pink RD Pst. Vat Red 1 C. I. #73360	7.51	7.51
Indanthrene Golden Orange G Dbl. Pst. Vat Orange 9 C. I. #59700	.135	.135
Sodium borohydride	.68	
Sodium hydroxide	28.80	60.00
Sodium hydrosulfite	13.10	60.00
Sodium chloride	75.60	

Table 4

[Shade: Green Cry 231. Goods: Cotton (5,000 yds.)]

Chemicals, etc.	A	B
	Pounds	*Pounds*
Jade Green N Supra Dbl. Pst. Vat Green 1 C. I. #59825	10.25	10.25
Ciba Yellow P2GA Dbl. Pst. Vat Yellow	5.78	5.78
Carbanthrene Brown BR Pst. Vat Brown 1 C. I. #70800	1.25	1.25
Sodium borohydride	.50	
Sodium hydroxide	23.00	51.00
Sodium hydrosulfite	8.60	51.00
Sodium chloride	43.70	

Table 5

[Shade: Pink. Goods: Cotton (4,600 yds.)]

Chemicals, etc.	A	B
	Pounds	*Pounds*
Indanthrene Red FBB Inf. Dbl. Pst. Vat Red 10 C.I. #67000	1.53	1.53
Ciba Yellow P2GA Dbl. Pst. Vat Yellow	.04	.04
Sodium borohydride	.96	
Sodium hydroxide	17.40	28.00
Sodium hydrosulfite	4.75	28.00
Sodium chloride	15.00	

Table 6

[Shade: Beige. Goods: Cotton (2,000 yds.)]

Chemicals, etc.	A	B
	Pounds	*Pounds*
Ciba Brown BGM Dbl. Pst. Vat Brown	0.90	0.90
Indanthrene Brown GG Infra Dbl. Pst. Vat Brown	0.76	0.76
Tinon Yellow P2GA Dbl. Pst. Vat Yellow	0.70	0.70
Sodium borohydride	0.58	
Sodium hydroxide	11.40	16.00
Sodium hydrosulfite	2.65	16.00
Sodium chloride	11.00	

Table 7

[Shade: Pink. Goods: Cotton (3,961 yds.)]

Chemicals, etc.	A	B
	Pounds	*Pounds*
Carbanthrene Red FBB Dbl. Pst. Vat Red 10 C.I. #67000	0.25	0.25
Ciba Yellow P2GA Dbl. Pst. Vat Yellow	0.09	0.09
Sodium borohydride	0.91	
Sodium hydroxide	13.20	28.00
Sodium hydrosulfite	4.55	28.00
Sodium chloride	18.00	

Table 8

[Shade: Avocado. Goods: Cotton (2,559 yds.)]

Chemicals, etc.	A	B
	Pounds	*Pounds*
Tinon Olive BFM Dbl. Pst. Vat Green 3 C.I. #69500	9.24	9.24
Ciba Yellow P2GA Dbl. Pst. Vat Yellow	13.10	13.10
Indanthrene Orange RRT Infra Pst. Vat Orange 1 C.I. #59705	.82	.82
Sodium borohydride	1.67	
Sodium hydroxide	27.00	33.00
Sodium hydrosulfite	5.80	33.00
Sodium chloride	30.00	

Table 9

[Shade: Creme de menthe. Goods: Cotton (10,000 yds.)]

Chemicals, etc.	A	B
	Pounds	*Pounds*
Jade Green Supra C Dbl. Pst. Vat Green 1 C.I. #59825	2.57	2.57
Ciba Yellow P2GA Dbl. Pst. Vat Yellow	2.45	2.45
Indanthrene Yellow Brown 3GI Pst. Vat Brown	1.80	1.80
Sodium borohydride	2.40	
Sodium hydroxide	45.00	69.00
Sodium hydrosulfite	11.70	69.00
Sodium chloride	47.00	

Table 10

[Shade: Green. Goods: Cotton (3,000 yds.)]

Chemicals, etc.	A	B
	Pounds	*Pounds*
Indanthrene Khaki GG Infra. Dbl. Pst. Vat #Green 8 C.I. 71050	6.65	6.65
Tinon Olive SFM Pst. Vat Black 25 C.I. #69525	2.80	2.80
Sodium borohydride	1.20	
Sodium hydroxide	27.00	33.00
Sodium hydrosulfite	6.00	33.00
Sodium chloride	15.00	

Table 11

[Shade: Green. Goods: Cotton (2,000 yds.)]

Chemicals, etc.	A	B
	Pounds	Pounds
Jade Green Supra C Dbl. Pst. Vat Green 1 C.I. #59825	30.80	30.80
Tinon Yellow GC Pst. Vat Yellow 2 C.I. #67300	6.58	6.58
Sodium borohydride	2.11	
Sodium hydroxide	33.00	42.00
Sodium hydrosulfite	8.10	42.00
Sodium chloride	33.33	

Table 12

[Shade: Mint mist. Goods: Cotton (10,000 yds.)]

Chemicals, etc.	A	B
	Pounds	*Pounds*
Jade Green Supra C Dbl. Pst. Vat Green 1 C.I. #59825	3.48	3.48
Ciba Yellow P2GA Dbl. Pst. Vat Yellow	1.58	1.58
Ciba Olive S Pst. Vat Black 25 C.I. #69525	.49	.49
Sodium borohydride	5.04	
Sodium hydroxide	45.00	96.00
Sodium hydrosulfite	18.50	96.00
Sodium chloride	45.00	

Table 13

[Shade: Charcoal. Goods: Cotton (5,000 yds.)]

Chemicals, etc.	A	B
	Pounds	*Pounds*
Tinon Olive SFM Pst. Vat Black 25 C.I. #69525	2.70	2.70
Indanthrene Grey GG Inf. Dbl. Pst. Vat Black 20	26.30	26.30
Ponsol Violet BNC Dbl. Pst. Vat Violet 13 C.I. #68700	27.00	27.00
Cibanone Red Brown RO Pst. Vat Brown 36	3.52	3.52
Sodium borohydride	.64	
Sodium hydroxide	24.00	56.00
Sodium hydrosulfite	3.15	56.00
Sodium chloride	77.00	

Table 14

[Shade: Blue. Goods: Cotton (4,000 yds.)]

Chemicals, etc.	A	B
	Pounds	*Pounds*
Ponsol Blue BFC Dbl. Pst. Vat Blue 6 C.I. #69825	3.92	3.92
Indanthrene Olive T Infra Pst. Vat Black 25 C.I. #69525	.41	.41
Jade Green Supra C Dbl. Pst. Vat Green 1 C.I. #59025	.06	.06
Sodium borohydride	.56	
Sodium hydroxide	21.60	42.00
Sodium hydrosulfite	2.75	42.00
Sodium chloride	45.90	

Table 15

[Shade: Aqua. Goods: Cotton (3,950 yds.)]

Chemicals, etc.	A	B
	Pounds	*Pounds*
Jade Green Supra C Dbl. Pst. Vat Green 1 C.I. #59825	4.33	4.33
Indanthrene Yellow-Brown 3G Infra Pst. Vat Brown	.23	.23
Sodium borohydride	.40	
Sodium hydroxide	15.00	24.00
Sodium hydrosulfite	1.95	24.00
Sodium chloride	32.40	

Table 16

[Shade: Gold. Goods: Cotton (23,650 yds.)]

Chemicals, etc.	A	B
	Pounds	*Pounds*
Indanthrene Orange RRT Infra Pst. Vat Orange 1 C.I. #59705	3.40	3.40
Ciba Yellow P2GA Dbl. Pst. Vat Yellow	163.35	163.35
Ciba Brown BGM Dbl. Pst. Vat Brown	39.92	39.92
Sodium borohydride	2.03	
Sodium hydroxide	110.40	234.0
Sodium hydrosulfite	40.55	234.0
Sodium chloride	263.90	

Table 17

[Shade: Mint mist. Goods: Cotton (10,000 yds.)]

Chemicals, etc.	A	B
	Pounds	*Pounds*
Jade Green N supra Dbl. Pst. Vat Green 1 C.I. #59825	4.35	4.35
Ciba Yellow P2GA Dbl. Pst. Vat Yellow	2.15	2.15
Indanthrene Olive T Infra Pst. Vat Black 25 C.I. #69525	.50	.50
Sodium borohydride	1.01	
Sodium hydroxide	42.00	96.00
Sodium hydrosulfite	19.20	96.00
Sodium chloride	116.10	

Table 18

[Shade: Hyacinth. Goods: Cotton (10,000 yds.)]

Chemicals, etc.	A	B
	Pounds	*Pounds*
Ponsol Blue BFC Dbl. Pst. Vat Blue 6 C.I. #69825	3.16	3.16
Brilliant Violet 3B Pst. Vat Violet 9 C.I. #60005	.25	.29
Sodium borohydride	1.08	
Sodium hydroxide	36.00	30.00
Sodium hydrosulfite	5.25	30.00
Sodium chloride	64.80	

Table 19

[Shade: Helio. Goods: Cotton (6,000 yds.)]

Chemicals, etc.	A	B
	Pounds	*Pounds*
Ponsol Violet BNC Dbl. Pst. Vat Violet 13 C.I. #68700	.23	.23
Ciba Violet 4 RR Dbl. Pst. Vat Violet 1 C.I. #60010	2.25	2.25
Carbanthrene Red FBB Dbl. Pst. Vat Red 10 C.I. #67000	1.41	1.41
Indanthrene Orange RRT Infra Pst. Vat Orange 1 C.I. #59705	.81	.81
Sodium borohydride	1.02	
Sodium hydroxide	35.00	90.00
Sodium hydrosulfite	6.25	90.00
Sodium chloride	66.00	

The synergism of the invention is directly related to air oxidation, which is, with respect to vat dyeing and other commercial hydrosulfite reducing operations, a function of time, temperature of the reducing bath, and the surface area of the reducing bath in contact with air. The synergism of the invention becomes markedly evident when the air oxidation reaches the potential encountered under commercial conditions of vat dyeing. Examples of commercial vat dyeing equipment where the air oxidation potential is sufficient to provide the most marked synergism are: Williams unit dyeing, pad steam dyeing, package dyeing, cascade dyeing, jig dyeing, etc. It is to be understood that the air oxidation potential in each of these processing techniques will vary as the conditions under which the dyeing procedure is conducted, vary.

Reference is now made to the following Tables A and B illustrating the synergistic effect provided by the present invention in the package dyeing of yarn as compared with conventional package dyeing of identical yarn and under the identical conditions of dyeing except for temperature. The package dyeing of the yarn in each instance was accomplished by placing the yarn package in the package dyeing machine where it was wet out by circulat-

ing an aqueous solution containing a conventional package dyeing wetting agent, for 10 minutes at 200° F. Only in the runs employing the conventional reducing procedure was a retardant, sodium lignin sulfonate, included in the wetting out operation. After the wetting operation, the vat dye pigment was circulated at 160° F. for 10 minutes. Alkali metal hydroxide was next added and circulated through the machine for 5 minutes at 160° F. In the runs wherein the reducing procedure of the present invention was employed sodium borohydride was added along with alkali metal hydroxide, after which all of the sodium hydrosulfite was added at the same time, and the resultant solution was circulated for 35 minutes to effect and maintain the desired reducing and dyeing. In the runs wherein conventional procedure was followed, half the hydrosulfite was added after the alkali metal hydroxide addition, and the resulting solution was circulated for 20 minutes after which the remainder of the hydrosulfite was added and the solution circulated for an additional 15 minutes. Following the dyeing operation, the yarn was rinsed, oxidized, soaped and softened in accordance with conventional package dyeing procedure. The comparative data are set forth below in the following tables:

Table A

Chemical, Etc.	Run No. 1		Run No. 2		Run No. 3	
	Invention	Conventional	Invention	Conventional	Invention	Conventional
30 S/2 Cotton, gms.	550	550	528.1	528.1	530	530
2 Ply Rayon, gms.	550	550	540	540	530	530
Sodium lignin sulfonate, gms.		6.75		6.75		6.75
Vat Blue 6 C.I. #69825, gms.	55.0	55.0				
Vat Green 1 C.I. #59825, gms.			54	54		
Vat Red 1 C.I. #73360, gms.					30.32	30.32
NaOH, gms.	12.5	66.0	12.5	66.0	37.0	66.0
$Na_2S_2O_4$, gms.	12.0	66.0	12.0	66.0	18.0	66.0
$NaBH_4$, gms.	2.52		1.8		2.4	
NaCl, gms.					20	
Reduction Temp., ° F.	160	160	200	160	195	160

Table B

Chemicals, Etc.	Run No. 4	
	Invention	Conventional
30 S/2 Cotton, gms.	569	569
2 Ply Rayon, gms.	565	565
Sodium lignin sulfonate, gms.		6.75
Vat Violet 1 C.I. #60010, gms.	22.34	22.34
Vat Blue 6 C.I. #69825, gms.	15.99	15.99
KOH, gms.	15.0	
NaOH, gms.		66
$Na_2S_2O_4$, gms.	18.0	66
$NaBH_4$, gms.	.72	
NaCl, gms.	10.0	
Reduction Temp., °F.	190	160

It will be noted from the foregoing comparative data that it is possible to achieve the same dyeing effect in accordance with the present invention as with conventional procedure, but with far lesser amounts of ingredients being required. It will also be noted that in accordance with the present invention a much higher temperature can be used. It will also be apparent that the reduction stability at high temperatures and control of electrolyte balance, afforded in accordance with the present invention, permit a more thoroughly penetrated yarn and a more uniformly controlled rate and degree of dye exhaustion.

A further very important feature of the invention resides in the ability to create and maintain a vat acid leuco by means of which textiles woven or formed of synthetic fibers and yarns may be dyed. Insofar as is known, the ability to dye the synthetics on a practical commercial scale in this manner has been considered commercially impossible.

In accordance with this aspect of the invention, reducing solutions as set forth in the following tables were prepared.

Table C

Sodium borohydride	percent	1.04
Sodium hydrosulfite	do	0.75
Vat Brown #1, C.I. #70800	do	2.00
Water		Balance
pH		9.5

The solution temperature was maintained at 190° F. and the fabrics were treated for 20 minutes therein. After dyeing the fabrics were rinsed in cold water, oxidized with sodium perborate, soaped at 200° F., rinsed and dried.

Table D

	Percent
Sodium borohydride	0.1
Sodium bisulfite	1.5
Vat Brown #1, C.I. #70800	2.5
Water	Balance

Ammonium hydroxide to provide pH 10.
Time—1 hour.

The same treatment after dyeing was used as in Table C.

Table E

	Percent
Sodium borohydride	0.1
Sulfurous acid	1.0
Vat Brown #1, C.I. #70800	2.0
Water	Balance

Ammonium hydroxide to provide pH 10.2.

The same treatment after dyeing was used as in Table C.

Fabrics woven of the following fibers were dyed in each of the above formulations: nylon, acetate, triacetate, acrylic, and polyester. In each case the fabric sample dyed a satisfactory brown shade.

It was further observed that by the addition of 3% benzyl alcohol to the procedure of Table C, the depth of shade and the rate of exhaustion were noticeably increased on nylon. An addition of 3% aniline emulsified in 2% of a commercially available nonylphenyl ethylene oxide condensate markedly increased the absorption of the acid leuco on polyester.

A further example of the effect of additives on vat acid leuco dyeing according to the invention is illustrated by the following table and procedure:

Table F

A reducing bath was prepared containing:

Sodium borohydride	percent	0.1
Cupric sulfate	do	0.3
Sodium hydrosulfite	do	1.5
Vat Green #1, C.I. #59825	do	0.5
Water		Balance
pH		9.5

A sample of acrylic fiber fabric immersed in this bath at 190° F. for one hour completely exhausted the bath and upon subsequent rinsing, oxidizing, soaping, and drying as previously outlined in Table C procedure, was dyed a satisfactory green shade.

The following examples illustrate package dyeing of synthetic textiles with the acid leuco vat dyeing technique as taught by the invention: 653 grams of nylon yarn were wet out and scoured in a one pound package machine in the conventional manner. The volume of water in the system was 10 liters. In a fresh bath at 140° F., 15 grams of a nonyl phenyl ethylene oxide condensate and 4% of Vat Brown #1, C.I. #70800, in pigment form on the weight of the fiber were added and circulated for 10 minutes. An addition was then made of 50 grams of benzyl alcohol. Circulation was carried out for a further 10 minutes at 140° F. A further addition was then made of ammonium hydroxide to give a pH of 10. Circulation was again continued for 10 minutes at 140° F. The temperature was then raised to 160° F. with then an addition of 1 gram of sodium borohydride followed by 15 grams of sodium hydrosulfite. Circulation was continued for 5 minutes and the temperature was raised to 180° F. Circulation was continued for 5 minutes and the temperature was raised to 190° F. Circulation continued for 30 minutes. The appearance of the bath at this point showed that substantial exhaustion of the dye had taken place and the bath was dropped. The packages were then rinsed, oxidized with sodium perborate, and soaped at 200° F. for 10 minutes in a manner similar to the like oxidation and soaping steps that would normally be conducted on a conventionally vat dyed cellulosic textile. Upon drying of the dyed nylon and comparing to a similar dyeing on cotton yarn the color and depth of shade were found to be similar. The nylon yarn dyed in this manner showed excellent washfastness and also good lightfastness.

Using similar procedure and equipment as the previous example: 580 grams of polyester yarn were dyed with 4% on the weight of the fiber of Vat Green #1, C.I. #59825, in the presence of 50 grams of methyl salicylate and 10 milliliters of 30% ammonium hydroxide. Fifteen grams of sodium hydrosulfite and ½ gram of sodium borohydride were used to effect and maintain reduction of the acid leuco form. Exhaustion of the bath was substantially complete in one hour at 2000° F. The fully oxidized and soaped shade was a bright turquoise, appreciably bluer and brighter than the shade of the same dye on cellulose. Washfastness and lightfastness of the resultant dyeing on the polyester were both good.

The method of the present invention may be employed in any form of localized vat dyeing such as flash ageing of printed textiles.

The textiles capable of being dyed with vat dyes in accordance with the invention may be any textile yarn or fiber or fabric made therefrom, both natural and synthetic, as well as blends. Other materials may also be dyed in accordance with the present invention, such as leather, cellulose pulp and solid bodies, shaped forms of synthetic polymers, like films and castings; and the like.

Another advantage of the invention lies in its effect on the reduction of azoic linkages, such as those present in a wide variety of dyes. It is possible, because of the inherent stability and/or synergism of the reducing action of the invention to color strip fabrics dyed with dyes containing azoic linkages using far lower quantities of hydrosulfite than heretofore possible. It should be further noted that in accordance with the present invention, color stripping of textiles dyed with azoic dyes does not degrade the textile to the same degree as conventional color stripping methods.

The present invention has been illustrated for use primarily in vat dyeing and stripping of vat dyes and of dyes containing azoic linkages. However, it will be readily apparent that the synergistic effect of the combination of

hydrosulfite and an alkali metal borohydride can be realized in any method wherein a material, chemically reducible by hydrosulfite, is reduced by hydrosulfite in the presence of air under conditions to cause, in the absence of the stabilizing effect provided by the borohydride in accordance with the present invention, air oxidation of a substantial portion of the hydrosulfite. The inclusion of the borohydride stabilizes the hydrosulfite against such air oxidation thereby affording the valuable advantages of the present invention.

Examples of hydrosulfite reductions, other than vat dyeing and stripping as illustrated above, in which the present invention may be practiced, are: bleaching of textiles, wood pulp, and the like; splitting of the cystine linkages in wool; reduction of metal salts and oxides as in the cleaning of surfaces of iron, stainless steel, lead, and the like, as well as in the cleaning of other surfaces stained with such salts or oxides; reduction of carbonyl groups to hydroxyl groups, such as on cellulose, or prevention of the formation of such carbonyl groups, thereby rendering the cellulose more resistant to oxidative deterioration.

The following specific examples illustrate the practice of the present invention in bleaching.

Table G

A reducing bath was prepared containing:

	Percent
Sodium borohydride	0.1
Sodium hydrosulfite	0.75
Ammonium hydroxide to pH 10.5.	
Water	Balance

Pieces of undyed, unbleached, scoured fabrics of cotton, rayon, nylon, polyester and acrylic were immersed under agitation in the bath at 175° F. for 30 minutes. They were then removed, rinsed and dried. The resulting fabrics were appreciably brighter and cleaner than originally. Following the same procedure but omitting the borohydride, the increase in brightness and cleanliness was not as marked, and the bath, after the 30 minute immersion, had suffered extensive hydrosulfite decomposition.

Table H

Desized and kier-boiled cotton fabric was impregnated with the following solution at a temperature of 90° F.:

	Percent
Sodium borohydride	0.08
Sodium hydrosulfite	0.25
Sodium hydroxide to pH of 12.	
Water	Balance

The fabric was then squeezed to a wet pick up of 80% and then placed under an infra red lamp at such a distance that the fabric was dried to about 10% moisture in 4 minutes. The resulting fabric was markedly whitened and brightened. The procedure was repeated but omitting the borohydride from the bath, and the resulting fabric was considerably less whitened and brightened. The procedure was also repeated but omitting the hydrosulfite from the bath. The resulting fabric was also considerably less whitened and brightened.

While there have been described herein what are at present considered preferred embodiments of the invention, it will be obvious to those skilled in the art that modifications and changes may be made therein without departing from the essence of the invention, the scope of which is defined in the appended claims, and that all modifications that come within the meaning and range of equivalency of the claims are intended to be included therein.

I claim:

1. In the dyeing of a material with a vat dye involving contacting said material with vat dye pigment and thereafter contacting said material with a hydrosulfite vat dye reducing medium, the improvement comprising the

step of providing in said hydrosulfite vat dye reducing medium an alkali metal borohydride and sufficient alkali metal hydroxide to provide a pH above 10 to provide the reduced vat dye in alkali leuco form, said vat dye reducing medium consisting essentially of said hydrosulfite, said alkali metal borohydride and said alkali metal hydroxide.

2. The method of claim 1 wherein the dye is exhausted into the material at a temperature between about 160° F. and boiling.

3. The method of claim 1 wherein said hydrosulfite is sodium hydrosulfite, wherein said alkali metal borohydride is sodium borohydride, and wherein said alkali metal hydroxide is sodium hydroxide.

4. The method of claim 7 wherein said hydrosulfite is sodium hydrosulfite; wherein said alkali metal borohydride is sodium borohydride, and wherein said alkali metal hydroxide is sodium hydroxide.

5. In a continuous method of dyeing a material with a vat dye which comprises passing said material into contact with a dispersion of a vat dye pigment, thereafter passing said material into contact with a hydrosulfite vat dye reducing medium, exhausting said dye in leuco form into said material, and thereafter contacting said material with an oxidizing agent, the improvement comprising the step of providing in said hydrosulfite vat dye reducing medium an alkali metal borohydride and sufficient alkali metal hydroxide to provide a pH above 10 to provide the reduced vat dye in alkali leuco form, said vat dye reducing medium consisting essentially of said hydrosulfite, said alkali metal borohydride and said alkali metal hydroxide.

6. The method of claim 5 wherein hydrosulfite and alkali metal borohydride are supplied to said vat dye reducing medium in amounts corresponding approximately to those of hydrosulfite and alkali metal borohydride being removed as such physically from said vat dye reducing medium by the passage of said material therethrough.

7. In the method of dyeing material with a vat dye in which the vat dye is reduced by a hydrosulfite reducing medium to leuco form and thereafter the material is contacted therewith, the improvement comprising the step of providing in said hydrosulfite reducing medium at the time of reduction, an alkali metal borohydride and sufficient alkali metal hydroxide to provide a pH above 10 to provide the reduced vat dye in alkali leuco form, said vat dye reducing medium consisting essentially of said hydrosulfite, said alkali metal borohydride and said alkali metal hydroxide.

8. In a method for removing color from a dyed material which comprises treating said dyed material with a solution of a hydrosulfite, the improvement which comprises the step of providing, in said hydrosulfite solution, an alkali metal borohydride and an alkali metal hydroxide to provide a pH of above 10, said solution consisting essentially of said hydrosulfite, said alkali metal borohydride and said alkali metal hydroxide.

9. In a method of reducing a unit amount of a vat dye with a given amount of hydrosulfite reducing agent, the improvement which comprises replacing a substantial portion of said hydrosulfite in the hydrosulfite reducing medium by an amount of an alkali metal borohydride substantially less than the amount equivalent to the amount of said replaced portion of hydrosulfite, there being sufficient alkali metal hydroxide in said hydrosulfite reducing medium at the time of reduction of the vat dye to provide a pH above 10 to provide said vat dye in alkali leuco form, said vat dye reducing medium consisting essentially of said hydrosulfite, said alkali metal borohydride and said alkali metal hydroxide.

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