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BRIGHT NICKEL PLATING COMPOSITIONS AND PROCESS

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This invention relates to the electrodeposition of the nickel group metals and is more particularly directed to nickel plating compositions including nickel plating baths, and to processes for electrodeposition of nickel, in which compositions (including plating baths) and processes a sulfuric acid reaction product of an alkyl-substituted-2-mercapto-dihydropyrimidine (or a salt of such sulfuric acid reaction product) and a sulfonated aryl aldehyde or salt thereof, or such sulfuric acid reaction product or salt thereof and a sulfonated aryl aldehyde and also a sulfonated aryl compound brightening agent free of the aldehyde group, are cooperatively used as a combination addition agent. The invention also relates to the articles obtained from operating the process.

While the invention is generally applicable to the electrodeposition of nickel group metals, as nickel, cobalt and iron, its immediate important applicability is in the direct electrodeposition of bright nickel. By direct electrodeposition of bright nickel, there is eliminated the need for buffing the plated article whether it is to be used as thus finished or to be provided with a further coat of chromium. Therefore, the invention may be conveniently illustrated by describing its use in nickel plating, although it is not restricted thereto.

In using a sulfuric acid reaction product of an alkyl-substituted-2-mercapto-dihydropyrimidine as an addition agent in the Watts type aqueous, acid nickel plating bath, such addition agent is only of limited value. For example, when it is used as the sole addition agent in such nickel plating bath and in a concentration which might give a bright deposit when operating the bath at a current density of 25 amperes per square foot, it is found that on dropping the current density to about 5 amperes per square foot, only a so-called semi-bright to dull deposit results. Likewise, upon changing the pH from a high value within the normal range of hydrogen ion concentrations observed in common commercial nickel plating to a lower value within such range, similar undesirable semi-bright to dull deposit is obtained.

Furthermore, in using a concentration of such sulfuric acid reaction product of an alkyl-substituted-2-mercapto-dihydropyrimidine as a sole

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addition agent in a concentration which might be sufficient to give a satisfactory overall bright deposit, the ductility is so poor that the deposit cracks readily on simply the slightest bending of the plate piece. Then, if the concentration of such addition agent is increased to give brilliance, the deposit is badly striated and inherently peels off from the base metal without outside initiation.

Thus, an ordinary acid Watts type nickel plating bath, in which such sulfuric acid reaction product of an alkyl-substituted-2-mercapto-dihydropyrimidine addition agent or salt thereof is the sole addition agent is undesirable for commercial bright nickel plating due to the narrow and uncertain operating limits, the formation of brittle and otherwise unreliable deposits, and the common probability of pitting, occurring.

According to the instant invention, it has been found that not only are these disadvantages overcome but also other advantages are gained by using as cooperating addition agents a sulfuric acid reaction product of an alkyl-substituted-2-mercapto-dihydropyrimidine or salt thereof together with preferably a sulfonated aryl aldehyde or salt thereof or with a sulfonated aryl compound brightening agent free of the aldehyde group or salt thereof, or together with both of these types of sulfonated brightening agents at the same time. Among the other advantages flowing from using together these cooperating agents is that when used together a smaller amount of each of them, and, as illustrated below, of both together is required to obtain the desirable results available from using them together than is required to obtain the specific results obtainable from the use of each of them separately.

These results and the invention may be illustrated, but not restricted to, the following examples which include the sodium salt of the product of the reaction of sulfuric acid with 2-mercapto-6-methyl-4,6-diethyl-dihydropyrimidine, hereinafter sometimes for brevity referred to as "agent A", as a particularly effective, specific example of the sulfuric acid reaction product of an alkyl-substituted-2-mercapto-dihydropyrimidine, and ortho-sulfobenzaldehyde sodium salt, hereinafter sometimes for brevity referred to as "agent C", as a specific example of the sulfonated aryl aldehyde. Thus, good bright

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nickel electrodeposits can be obtained directly by employing the indicated operating conditions in the following baths, and which deposits possess good ductility.

	range	optimum
nickel sulfate (7H ₂ O)	27 to 45	37 ounces per gallon.
nickel chloride (6H ₂ O)	6 to 9	8 ounces per gallon.
boric acid	4.5 to 8	5 ounces per gallon.
agent C	3 to 8	5 grams per liter.
pH (electrometric)	3.5 to 5.5	5.0.
temperature	110° to 130°	120° Fahrenheit.
current density	1.5 to 100	25 amperes per square foot—average.

Under certain circumstances, at certain indicated conditions, by using agent C in the range of one to three grams per liter or at an optimum amount of 1.5 grams per liter, there can be obtained a semi-bright nickel deposit, often referred to as "blushed" or "milky", that is, having the appearance of a mirrored surface that had been breathed upon and requiring only slight buffing to produce a bright or mirror-like finish.

Moreover, if agent A is used alone in a range of 0.5 to 2.0 (or optimum 1.0) gram per liter entirely to replace agent C in the above baths under the indicated operating conditions but employing an optimum pH of 4.0 and current density range of 10 to 100 amperes per square foot (optimum 50), the undesirable results noted in the third and fourth paragraphs in column 1 hereof are obtained.

On the other hand, if instead of the indicated range and optimum amount of agent C recited above, there is used as little as from 0.5 to 3 (or optimum 1.0) grams per liter of it but together with as little as 0.005 to 0.015 (optimum 0.012) gram per liter of agent A, an improved bright nickel deposit over that obtainable by using agent C alone results, for example, a brilliant nickel ductile deposit occurs immediately on buffed brass and persists also at all thicknesses of the deposit and is also obtained over unbuffed copper deposits on die-castings. The baths containing these combined cooperating agents also give direct bright and ductile nickel deposits over bright dipped brass having soldered parts as well as over unbuffed copper plated steel and a brilliant deposit in barrel plating bright dipped brass. All the here noted deposits are highly ductile.

While in the example the invention is illustrated in an aqueous bath containing both nickel chloride and sulfate, it is also applicable in an aqueous, acid bath containing nickel ion yielding material selected from nickel sulfate and nickel chloride alone as well as mixtures of them.

While agent A is included as an unusually effective example of a product of the reaction of sulfuric acid with an alkyl-substituted-mercapto-dihydropyrimidine, the products of the reaction of sulfuric acid with other such alkyl-substituted-mercapto-dihydropyrimidines, the type and preparation of which is shown in U. S. Patent No. 2,234,848 issued March 11, 1941, may be likewise employed in the practice of the invention.

The product of the reaction of sulfuric acid with, or the sulfuric acid reaction product of, the alkyl - substituted - mercapto - dihydropyrimidines may be prepared by suitable treatment of the selected starting thus-substituted-pyrimidine with the desired form of sulfuric acid, and may be illustrated by, but not restricted to, the following preparation of agent A:

300 grams of 2-mercapto-6-methyl-4,6-diethyl-

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dihydropyrimidine are added slowly to 600 c. c. of 95% sulfuric acid while the mixture is stirred and cooled to maintain its temperature within the range from about 20° to about 40° C., until no more heat is evolved. The solution is then warmed until evolution of sulfur dioxide gas ends. The mixture is then cooled and to it is added a suspension of 600 grams of calcium hydroxide in 3 liters of water, which should be enough lime to precipitate all of the free sulfuric acid as calcium sulfate and to form the soluble calcium salt of the sulfonated or sulfated mercapto pyrimidine derivative. This calcium salt is then converted to the sodium salt by the addition of sodium carbonate solution to the filtrate until there is no further precipitation of calcium carbonate which is then removed by filtration. The filtrate containing the sodium salt of the sulfuric acid reaction product is evaporated until it becomes a pale yellow to white powdery crystalline mass which is water soluble. Other metal salts, if desired, may be prepared by treating an aqueous solution of the sodium or calcium salt with a salt of the desired metal in known manner.

Thus, the addition agent of which agent A is a preferred example may be most generally referred to as a sulfuric acid reaction product of an alkyl-substituted-mercapto-dihydropyrimidine or less broadly, of an alkyl-substituted-2-mercapto-dihydropyrimidine. The more effective of these sulfuric acid reaction products are of the 2-mercapto - 4,6 - alkyl - substituted - dihydropyrimidines and more so of the 2-mercapto-4-alkyl-6-dialkyl-dihydropyrimidines. They are generally referred to as the product of the reaction of sulfuric acid with, or the sulfuric acid reaction product of, trialkyl-mercapto-pyrimidines because they are believed to be either sulfonated or possibly sulfated products, or mixtures thereof of these pyrimidines.

The sulfonated aryl aldehydes useful in the cooperative combination addition agent of the invention may be selected from such as the mono- or poly-sulfonated mono- or poly-nuclear aryl aldehydes, of which the polynuclear type is exemplified by the sulfonated anthraldehydes or naphthaldehydes, and of which specially desired are the mono-nuclear derivatives, among which sulfonated cinnamaldehyde illustrates the unsaturated alkyl or vinyl type, and others are exemplified by sulfonated salicylaldehyde and other sulfonated benzaldehydes, including the saturated alkylated compounds such as tolualdehyde, and especially the non-alkylated type as the various sulfobenzaldehydes such as the mono-sulfobenzaldehydes as ortho-, meta- and para-sulfobenzaldehyde, or the alkoxyated derivatives as in sulfonated para-methoxy benzaldehyde (anisaldehyde), or the poly or disulfobenzaldehydes as the nickel salt of 2,5-disulfobenzaldehyde illustrating the polysulfonated form, any of which may be employed either as the free sulfonic acid derivative or as a salt thereof such as that obtained by replacing the hydrogen of the sulfonic acid radical by its equivalent of a salt forming cation such as a metal, for example, an alkali metal as sodium or potassium, or an alkaline earth metal as magnesium or a nickel group metal as nickel, cobalt or iron, or an amine type cation including ammonium and those derived from amines or alkylamines as methyl- or ethylamine, or from an alkylolamine as mono-, di- or triethanolamine, or other suitable salt forming base, all of which free acid or salt form of the sulfonated aryl aldehydes may be broadly re-

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ferred to in this specification and in the claims as a sulfonated aryl aldehyde or sulfonated aryl aldehydes.

While the advantages available from the compositions (including the plating baths) and the processes of this invention are particularly exhibited by the compositions and processes, in which the trialkyl-substituted-2-mercapto-dihydropyrimidine and the sulfonated aryl aldehyde are used together as the cooperating combination addition agent, good results of the type indicated follow also when the trialkyl-substituted-2-mercapto-dihydropyrimidine and a sulfonated aryl compound brightening agent free of the aldehyde group are used together as the components of the cooperating combination addition agent. Satisfactory results are also obtained when all three classes of these agents are represented as components at the same time in the combination addition agent.

Suitable examples of the sulfonated aryl compound brightening agent free of the aldehyde group are such as the mono- or poly-sulfonated mono- or poly-nuclear aromatic compound containing either the benzene or naphthalene nucleus, such as the benzene sulfonic acids, benzene disulfonic acids, toluidine sulfonic acids, toluidine disulfonic acids, naphthalene sulfonic acids, naphthol sulfonic acids, naphthylamine sulfonic acids, or mildly chlorinated derivatives of such sulfonic acids, of which examples include also alpha and beta naphthalene mono-sulfonic acids, the 1,5- and 2,7-naphthalene disulfonic acids, alpha naphthylamine trisulfonic acid, 2-amino-toluene-5-sulfonic acid, 2-amino-toluene-4-sulfonic acid, 4-amino-toluene-2-sulfonic acid, ortho-toluidine disulfonic acid, and naphthalene-1,5-disodium sulfonate, all of which may be employed as the free sulfonic acid or a salt thereof such as that obtained by replacing the hydrogen of the sulfonic acid radical by its equivalent of a salt forming cation of the type described at column 4, line 64 to column 5, line 2 hereof, all of which free acid or salt forms of such sulfonated aryl compound may be broadly referred to herein and in the claims as a sulfonated aryl compound brightening agent free of the aldehyde group, sometimes for brevity referred to herein as "agent B."

A Watts bath containing nickel sulfate and chloride and boric acid in the ranges indicated at column 3 hereof and per liter from about 0.02 to about 0.50 gram of agent A together with from about one to about ten grams of a sulfonated aryl compound brightening agent free of the aldehyde group such as naphthalene 1,5-disodium sulfonate, operated at the ranges of temperature, pH and current density there shown yields a bright nickel deposit with good hiding and covering power, and surprisingly good ductility. Where necessary in this combination to lower the surface tension, a compatible wetting agent, such as technical sodium lauryl sulfate may be added, for example, at about 1.0 gram per liter.

The substance of the type of agent A may be employed in an amount between about 0.005 and about 0.015 gram per liter together with a substance of the sulfonated aryl aldehyde type as agent C at least one gram per liter and preferably at least 2 grams per liter over a wide range of pH and preferably at pH from about 2.5 to about 4.5, although not restricted thereto. On highly buffed basis metal surfaces, the resulting nickel deposit is brilliant and indicates good power to hide base metal imperfections even with

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deposits of thickness less than 0.0002 inch, thus showing evidence of good hiding power. On unbuffed basis metals, unbuffed copper and matte surface basis metal, the deposit is bright to brilliant depending on the thickness of the deposit. The nickel deposit is distinctly silver-like in color and free of any yellow tinge.

The use of the cooperating combination addition agents of this invention gives an extremely bright, surprisingly ductile, very adherent plate with exceptionally good hiding power.

The influence of the presence of the sulfonated aryl aldehyde avoids the necessity for a wetting agent, although one may be used if at any time it is desired to lower the surface tension.

The unusual hiding power obtained by the use of the cooperating addition agents herein permits an elegant deposit directly on steel, even on a poor grade of steel, and also without pre-plating with copper or polishing or buffing. It makes it possible to plate all poorly finished surfaces and directly on unbuffed copper, zinc die-castings, bright-dipped surfaces as well as matte surfaces, also on brass, copper, copper-plated zinc die-castings and on nickel plated zinc die-castings. In decorative plating where thickness of nickel is not of extreme importance, a real brilliant deposit can be built up in the shortest time.

The use of the substance of the type of agent A in the combination permits saving plating time, and current and anode consumption. No agitation of the bath is required and a minimum of supervision and of a simple order is necessary. The combination exhibits unusual throwing power enabling the deposit to reach and adequately and uniformly cover the most intricate surfaces and the innermost exposed surfaces of the oddest shaped articles.

The plating compositions of the invention may be prepared for offering to the trade, containing all of the constituents in the same concentrations in which they respectively occur in the plating bath as actually used, or in a suitable higher concentration up to that containing the cooperating combination addition agents in the concentration of their saturated solutions, and either with or without the nickel ion yielding material included in the composition.

Thus, for preparing a nickel plating bath for operation according to the invention, there may be offered to the trade a so-called make-up solution containing, for example, 36 grams of agent A per gallon of water and agent C and/or agent B in the corresponding relative amount to that in which they are used in the plating bath as it is to be operated. In the initial make-up of the bath about a pint of this solution is required per one hundred gallons of plating bath. After the bath has thus been in operation for some time and may require some addition of the cooperating agents, the same or similar solution may be used as a replenishment solution, for example, at about twenty-five to thirty-five cubic centimeters per one thousand ampere hours of plating.

In a bath in which it is contemplated to use a substance of the type of agent A along with one of the type of agent B and without or even with agent C, the agent B such as naphthalene-1,5-disodium sulfonate may be used, for example, in relation to the composition indicated in the second paragraph in column 3 hereof, in a concentration of about 0.5 to about 2.0 grams per liter, and optimum about 1.0 gram per liter.

While the invention has been illustrated by reference to certain specific embodiments of it,

It is understood that many modifications, alterations, substitutions and equivalents of the various combinations may be employed within the scope of the appending claims as considered in view of the prior art.

What is claimed is:

1. A nickel electroplating bath addition agent composition comprising a nickel electrodeposit brightening agent consisting essentially of (I) a sulfonated aryl aldehyde and (II) a sulfuric acid reaction product of an alkyl-substituted-mercapto-dihydropyrimidine, said reaction product resulting from reacting an alkyl-substituted 2-mercapto dihydropyrimidine with concentrated sulfuric acid with accompanying evolution of sulfur dioxide from the reaction mixture which is heated until such evolution has substantially ceased, and having the aldehyde (I) and the reaction product (II) in the ratio of from about 0.5 to about 3.0 parts of the aldehyde (I) to from about 0.005 to about 0.02 part of the product (II), said addition agent composition being capable, upon addition to an aqueous, acid nickel plating bath comprising in solution in its aqueous medium a nickel ion-yielding material consisting essentially of a mixture of nickel sulfate and nickel chloride, of causing a bright, ductile cathodic deposit of nickel to be obtained upon passing an electric current from the anode through said bath to the cathode when the sulfonated aldehyde and the sulfuric acid reaction product of the substituted-mercapto-pyrimidine are present in the bath respectively in combined, cooperative quantities sufficient to permit the bright, ductile deposit of nickel to be obtained under the operating conditions.
2. A nickel electroplating bath addition agent composition as claimed in claim 1, in which the sulfuric acid reaction product of the substituted-mercapto-pyrimidine is a sulfuric acid reaction product of a 2-mercapto-trialkylated-dihydropyrimidine and the sulfonated aryl aldehyde is a mononuclear sulfonated benzaldehyde.
3. A nickel electroplating bath addition agent composition as claimed in claim 1, in which the sulfuric acid reaction product of the substituted-mercapto-pyrimidine is a sulfuric acid reaction product of a 2-mercapto-6-alkyl-4,6-dialkyl-dihydropyrimidine and the sulfonated aryl aldehyde is a sulfonated benzaldehyde.
4. A nickel electroplating bath addition agent composition as claimed in claim 1, in which the sulfuric acid reaction product of the substituted-mercapto-pyrimidine is a sulfuric acid reaction product of 2-mercapto-6-methyl-4,6-diethyl-dihydroxypyrimidine and the sulfonated aryl aldehyde is a monosulfobenzaldehyde.
5. A nickel electroplating bath addition agent composition as claimed in claim 1, in which the sulfuric acid reaction product of the substituted-mercapto-pyrimidine is a sulfuric acid reaction product of 2-mercapto-6-methyl-4,6-diethyl-dihydroxypyrimidine and the sulfonated aryl aldehyde is ortho-sulfobenzaldehyde.
6. A nickel electroplating bath addition agent composition as claimed in claim 1, in which the sulfuric acid reaction product of the substituted-mercapto-pyrimidine is a sulfuric acid reaction product of 2-mercapto-6-methyl-4,6-diethyl-dihydroxypyrimidine and the sulfonated aryl aldehyde is sulfonated cinnamaldehyde.
7. An acid, aqueous electroplating bath for nickel electroplating, which bath comprises in solution in its aqueous medium a nickel ion-yielding material consisting essentially of a member of

- the class consisting of nickel sulfate, nickel chloride, and a mixture of nickel sulfate and nickel chloride, said bath having the capability of permitting a bright, ductile, cathodic electrodeposit of nickel to be deposited under the operating conditions upon the passage of an electric current through the bath, said bath having said capability imparted to it by the inclusion therein of cooperating addition, brightening agents consisting essentially of (I) the sulfuric acid reaction product of an alkyl-substituted-2-mercapto-dihydropyrimidine said reaction product resulting from reacting an alkyl-substituted 2-mercapto dihydropyrimidine with concentrated sulfuric acid with accompanying evolution of sulfur dioxide from the reaction mixture which is heated until such evolution has substantially ceased, and (II) a sulfonated aryl aldehyde, each of said agents I and II being present respectively in a quantity relative to the other sufficient to permit the bright, ductile nickel electrodeposit having good hiding power to be deposited directly on the cathode, and with agent I present at a concentration of under 0.5 gram per liter and even as little as about 0.005 gram per liter and agent II at about 3.0 grams per liter and less.
8. An acid, aqueous electroplating bath as claimed in claim 7, in which the 2-mercapto-dihydropyrimidine is a trialkyl-substituted-2-mercapto-dihydroxypyrimidine.
 9. An acid, aqueous electroplating bath as claimed in claim 7, in which the 2-mercapto-dihydroxypyrimidine is a 6-alkyl-4,6-dialkyl-2-mercapto-dihydroxypyrimidine.
 10. An acid, aqueous electroplating bath as claimed in claim 7, in which the 2-mercapto-dihydroxypyrimidine is a 2-mercapto-6-alkyl-4,6-dialkyl-dihydroxypyrimidine and the sulfonated aryl aldehyde is a sulfonated mononuclear aryl aldehyde.
 11. An acid, aqueous electroplating bath as claimed in claim 7, in which the 2-mercapto-dihydroxypyrimidine is a 2-mercapto-6-alkyl-4,6-dialkyl-dihydroxypyrimidine and the sulfonated aryl aldehyde is a sulfonated benzaldehyde.
 12. An acid, aqueous electroplating bath as claimed in claim 7, in which the 2-mercapto-dihydroxypyrimidine is 2-mercapto-6-methyl-4,6-diethyl-dihydroxypyrimidine and the sulfonated aryl aldehyde is a sulfonated phenyl aldehyde.
 13. An acid, aqueous electroplating bath as claimed in claim 7, in which the 2-mercapto-dihydroxypyrimidine is 2-mercapto-6-methyl-4,6-diethyl-dihydroxypyrimidine and the sulfonated aryl aldehyde is a sulfonated mononuclear aryl aldehyde.
 14. An acid, aqueous electroplating bath as claimed in claim 7, in which the 2-mercapto-dihydroxypyrimidine is 2-mercapto-6-methyl-4,6-diethyl-dihydroxypyrimidine and the sulfonated aryl aldehyde is a monosulfo-benzaldehyde.
 15. An acid, aqueous electroplating bath as claimed in claim 7, in which the 2-mercapto-dihydroxypyrimidine is 2-mercapto-6-methyl-4,6-diethyl-dihydroxypyrimidine and the sulfonated aryl aldehyde is a sulfonated benzaldehyde.
 16. An acid, aqueous electroplating bath as claimed in claim 7, in which the 2-mercapto-dihydroxypyrimidine is 2-mercapto-6-methyl-4,6-diethyl-dihydroxypyrimidine and the sulfonated aryl aldehyde is ortho-sulfobenzaldehyde.
 17. An acid, aqueous electroplating bath as claimed in claim 7, in which the 2-mercapto-dihydroxypyrimidine is 2-mercapto-6-methyl-4,6-

diethyl-dihydroxypyrimidine and the sulfonated aryl aldehyde is sulfonated cinnamaldehyde.

18. The method of electroplating a bright, ductile, cathodic deposit of nickel directly from a plating bath for nickel electro-deposition, which bath comprises in solution in its aqueous medium a nickel ion-yielding material consisting essentially of a member of the class consisting of (a) nickel sulfate, (b) nickel chloride, and (c) a mixture of nickel sulfate and nickel chloride, which method comprises passing an electric current from the anode through said bath to the cathode, in the presence in said bath of cooperating addition, brightening agents consisting essentially of (I) the sulfuric acid reaction product of a trialkyl-substituted - 2 - mercapto - dihydroxypyrimidine said reaction product resulting from reacting an alkyl-substituted 2-mercapto dihydroxypyrimidine with concentrated sulfuric acid with accompanying evolution of sulfur dioxide from the reaction mixture which is heated until such evolution has substantially ceased, and (II) a sulfonated aryl aldehyde, each of said two agents being present in a quantity relative to the other sufficient to permit the bright, ductile nickel electrodeposit having good hiding power to be deposited directly on the cathode with agent I present at a concentration of under 0.5 gram per liter and even at as little as about 0.005 gram per liter and agent II at about 3.0 grams per liter and less.

19. The method as claimed in claim 18, in which the 2-mercapto-dihydroxypyrimidine is a 6-alkyl-4,6-dialkyl-2-mercapto-dihydroxypyrimidine.

20. The method as claimed in claim 18, in which the 2-mercapto-dihydroxypyrimidine is 2-mercapto-6-methyl-4,6-diethyl-dihydroxypyrimidine and the sulfonated aryl aldehyde is a sulfonated mononuclear aryl aldehyde.

21. The method as claimed in claim 18, in which the 2-mercapto-dihydroxypyrimidine is 2-mer-

capto-6-methyl-4,6-diethyl-dihydroxypyrimidine and the sulfonated aryl aldehyde is sulfonated phenyl aldehyde.

22. The method as claimed in claim 18, in which the 2-mercapto-dihydroxypyrimidine is 2-mercapto-6-methyl-4,6-diethyl-dihydroxypyrimidine and the sulfonated aryl aldehyde is a sulfonated benzaldehyde.

23. The method as claimed in claim 18, in which the 2-mercapto-dihydroxypyrimidine is 2-mercapto-6-methyl-4,6-diethyl-dihydroxypyrimidine and the sulfonated aryl aldehyde is a monosulfobenzaldehyde.

24. The method as claimed in claim 18, in which the 2-mercapto-dihydroxypyrimidine is 2-mercapto-6-methyl-4,6-diethyl-dihydroxypyrimidine and the sulfonated aryl aldehyde is ortho-sulfobenzaldehyde.

25. The method as claimed in claim 18, in which the 2-mercapto-dihydroxypyrimidine is 2-mercapto-6-methyl-4,6-diethyl-dihydroxypyrimidine and the sulfonated aryl aldehyde is sulfonated cinnamaldehyde.

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