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DYEING PROTEINACEOUS AND NYLON MATERIALS

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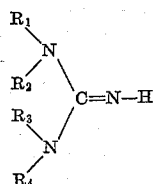
20 Claims. (Cl. 8-54)

This invention relates to compositions and methods for dyeing proteinaceous and nylon materials and more particularly to compositions and methods utilizing high affinity wool dyes.

The high affinity wool dyes, which are sometimes referred to as milling colors or neutral dyeing acid dyes, have several advantages and in particular have the advantage that they generally result in colors which are reasonably fast to washing. Unfortunately dyes of this class have the severe disadvantage that they are not level dyeing colors and the use of such dyes frequently results in objectionable area or fiber shading.

Numerous efforts have been made in the past to develop level dyeing procedures utilizing the milling colors. For example, it is suggested in U.S. Patent 2,590,847 that an ammonium salt be added to the dye bath so that as the salt decomposes, the pH of the dye bath is gradually lowered and the dye is slowly and uniformly exhausted onto the textile material. This procedure is undoubtedly an improvement over the prior art practice of adjusting the pH by acid additions but it is now apparent that pH control is not the complete solution to the problem of obtaining level shades with milling colors. It has also been suggested (Journal Society of Dyers and Colourists, page 297, volume 64, 1948) that dyeings with milling colors might be started at the boil instead of starting the dyeing at a low temperature and gradually raising the temperature of dye bath to the boil in a conventional manner. The high initial temperatures in this suggested process apparently decrease the dye particle size and increase fiber swelling and this should be conducive to level dyeing. While the procedure undoubtedly has some merit, it is difficult to practice and fails to give satisfactory results in a large number of instances.

It has now been found according to this invention that even under exceedingly adverse conditions, level shades can be obtained with milling colors by adding to the dye bath a compound selected from the group consisting of bases represented by the formula:



wherein R_1 , R_2 and R_3 represent members selected from the group consisting of hydrogen, monocyclic aromatic radicals, aliphatic radicals, and cycloalkyl radicals, and R_4 represents a radical selected from the group consisting of

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monocyclic aromatic, aliphatic and cycloalkyl radicals; and acid addition salts thereof.

The nature of the members R_1 to R_4 inclusive may vary within reasonably wide limits although strongly hydrophobic substituents are preferred and best results are usually obtained when the total effect of the four groups is such as to reduce the solubility of the free base to such a value that it is not completely soluble in the dye bath at the concentration employed. Typical substituent groups which may be represented by R_1 to R_4 include phenyl, tolyl, cyclohexyl, benzyl, and aliphatic hydrocarbon radicals having from 1 to 25 carbon atoms as illustrated by butyl, dodecyl, stearyl and allyl radicals. Illustrations of specific compounds which may be employed are sym.-diphenylguanidine, sym.-o-ditolylguanidine, $\alpha,\alpha,\gamma,\gamma$ -tetramethylguanidine, α,α -diphenylguanidine, α -phenylguanidine, sym.-dibenzylguanidine, α -cyclohexylguanidine, and α -dodecylguanidine. Sym.-diphenylguanidine is the presently preferred reagent primarily because it is readily available and low in cost.

The process of this invention is useful in any instance where unevenness is or may be encountered when employing the high affinity or milling dyes on proteinaceous or nylon materials. Frequently more difficulty is encountered when employing a given milling dyestuff on one type of fiber than when employing the same dyestuff on other fibers, and, for example, dyestuffs which give a reasonably level shade upon wool by conventional expedients give an extreme degree of unevenness upon chlorinated woollens. Not only will the chlorinated wool be dyed more heavily near the tips of the fibers but area shading will be apparent throughout the dyed fabric. Likewise, uneven dyeing is frequently a greater problem with nylon rugs or the like than with plain weave fabrics. The process of this invention will alleviate tippy dyeing and/or area shading even with chlorinated woollens and nylon pile fabrics and makes an even shade more readily obtainable in any instance where a milling color is employed.

The milling colors do not constitute a precise class of dyes but are generally considered to be a part of the class of dyestuffs known as "acid dyes." They differ from the more conventional acid dyes in that they result in a greater degree of fastness to milling or alkaline scouring and also differ in that they exhaust from the dye bath at a higher pH. Generally the higher the pH at which the dye will exhaust, the greater the degree of wash fastness and the greater the tendency of the dye to give uneven shading. There is no sharp dividing line between the milling colors and conventional acid dyes, but since any dyestuff which gives a satisfactory degree of exhaustion at or above a pH of about 5 displays a measure of fastness to milling and generally gives difficulties with shading, it is intended that "milling colors" be defined, for the purposes of this specification, to include all such dyes. It is also intended that "milling colors" include certain direct dyes for cottons which can be used as neutral dyeing colors for wool or the like, and certain neutral dyeing colors which are best used with a mordant. The following is a representative list of dyestuffs with which the invention will be found to be useful: Milling Yellow H5GA (PR. 138), Polar Yellow 2G Conc. (C.I. 642), Cloth Fast Yellow RS (PR. 187), Irgalan Brown 2GL (Geigy), Xylene Milling Red G (C.I. 443), Nylanthrene Scarlet YLFW (Althouse Chemical Company), Erie Scarlet B 110%

(C.I. 382), Crocein Scarlet N EX. (C.I. 252), Anthraquinone Violet D (C.I. 1080), Erio Anthracene Cyanine 2RL (Geigy), Pontacyl Fast Blue SB 150% (C.I. 209), Supramine Pure Blue BL (General Dyestuff Corporation), Carbolan Brilliant Blue 2R Conc. (Arnold, Hoffman), Brilliant Indocyanine 6B A (PR. 222), Genalan Brilliant Blue BCF (General Dyestuff Corporation), Supernylite Blue BR (Althouse Chemical Company), Alizarine Cyanine Green G EX. (C.I. 1078) Pontachrome Fast Grey L (PR. 206). Many of the above dyes represent one of a general class made by a given manufacturer and in such instances the invention is useful with the entire class.

The amount of the dyestuff employed may be conventional and depends upon the color and shade desired. For very light shades it is frequently necessary to employ only a small fraction of one percent, based on the weight of goods, of dyestuff and frequently dyeings are conducted employing 0.02% or less dyestuff. On the other hand, an excellent black can generally be obtained employing only about 6% dyestuff so that there is seldom any advantage in using a greater quantity of dye, although in infrequent instances the amount of dyestuff employed may be as high as 10% or 15% based on the weight of goods to be dyed.

The amount of the guanidine type compound employed may be varied within wide limits. For example, satisfactory results can sometimes be achieved when employing as much as 10 to 15% of the guanidine compound based upon the weight of material to be dyed, but the use of such large amounts is wasteful and in some instances adversely affects the hand of the dyed fabric. Generally there is no advantage in using more than about 4% of the guanidine compound on the weight of the material to be dyed and the preferred upper limit is 2% on the weight of the goods. Much smaller amounts can frequently be employed and in some instances it has been observed that unevenness can be eliminated by employing as little as 0.1%, based on the weight of goods, of the guanidine compound. Generally, however, when dyeing other than very light shades, it is advantageous to employ at least about 0.25% of the guanidine compound on the weight of the goods since any reasonable excess over the minimum amount required does not adversely affect the efficiency of the dyeing nor the hand of the dyed fabric.

The guanidine compound is preferably insoluble in a basic dye bath in the concentrations employed so that it is usually necessary to employ the same in the form of a dispersion. The dispersion can be formed in any manner and the only requirement is that the dispersion be reasonably stable during the dyeing operation. For example, the guanidine compound in the form of its acid addition salt may be dissolved in a small amount of water, preferably containing a suitable dispersing agent, and the solution can thereafter be neutralized with sodium hydroxide or other base to result in precipitation of the free guanidine base in the form of finely dispersed particles. Alternatively one can employ a colloidal mill or the like for producing a concentrated dispersion which can thereafter be added to the dye bath. The preferred method for forming the dispersion, however, comprises dissolving the free guanidine base in a large quantity of a suitable dispersing agent and thereafter adding this solution to the dye bath. Any anionic or nonionic dispersing agent capable of acting as a solvent for the guanidine base may be employed for this purpose, and the following are only illustrative examples: highly sulfonated castor oil, sodium 1-isobutyl-4-ethyloctyl sulfate, mono-p-nonylphenyl ether of hexaethylene glycol, sodium mono-p-octylphenyl ether of diethylene glycol sulfate. The preferred dispersing agent when employing such a procedure comprises sulfonated castor oil since this dispersing agent has a leveling effect upon milling colors in itself and supplements the leveling action of the guanidine compound. The guanidine compounds are, how-

ever, not sufficiently soluble in sulfonated castor oil to permit, in some instances, the use of this dispersing agent alone. Such a large amount of the castor oil derivative would be required that it might affect the hand of the goods, and, for this reason, it is generally advantageous to employ approximately equal parts of sulfonated castor oil and a second compound in which the guanidine compounds has a greater solubility, such as an alkylaryl polyether sulfate dispersing agent. It is also generally advantageous to employ the minimum amount of the dispersing agent mixture in which the guanidine compound is soluble or, in other words, about 4 to 12 parts of dispersing agent for each part of the guanidine compound. A satisfactory procedure comprises mixing together the two dispersing agents, adding the guanidine compound, warming the mixture until the guanidine compound is completely dissolved and thereafter adding the solution to the dye bath with agitation.

The improvement of this invention can be incorporated into any conventional dyeing procedure with the milling colors including the high initial temperature procedure discussed above. The preferred procedure, however, comprises dispersing the guanidine compound in a dye bath equal in weight to from about 10 to 60 times and preferably from 20 to 40 times the weight of the goods to be dyed, adjusting the temperature of the bath, adding the goods, and after about 5 or more minutes to allow the goods to be thoroughly wet by the bath, adding the dyestuff. The temperature of the bath at the time the goods and dyestuff are entered may vary from room temperature to the boiling point of the bath or even higher if pressure equipment is employed, but since a low temperature assists in reducing the initial dye strike or, in other words, the amount of the dye that is exhausted onto the fabric in the first few minutes of dyeing, and since a high temperature according to this invention is not required to break up the dye agglomerates, a low temperature for entering the goods and the dyestuff into the bath is generally advantageous. On the other hand, a suitable dispersion of the guanidine compound can, as a general rule, be more readily made if the dye bath is slightly warmed before the guanidine is added. With regard to both of these considerations, the dye bath may advantageously be at a temperature of from about 70 to 150° F. and is preferably at a temperature of from about 80 to 110° F. at the time the goods are entered therein and the dyestuff is added.

While the temperature of the bath has some affect upon the initial dye strike, the initial pH of the dyebath is the most important factor influencing this variable and is also important for other reasons. If the initial pH of the dye bath is too low, the initial dye strike will be so great that an uneven dyeing might result, and if the pH of the dye bath is too high, damage to goods may result. As a general rule the pH should be high enough so that not more than 40% and preferably not more than 20% of the dyestuff exhausts upon the fabric during the first 10 minutes of the dyeing cycle and while the exact pH required for this result will vary depending upon the temperature of the bath, the particular color or colors employed and the type of goods being dyed, as a general rule an initial dye bath pH of at least about 7 will give satisfactory results. An initial dye bath pH of 10 or higher may be employed with nylons but the initial pH should not be above about pH 8 with wool containing materials since above this value there is danger that the wool might be damaged. In many instances, the pH of the dye bath as prepared is such that pH adjustment is not required, but if such is found to be necessary, the pH of the bath can readily be brought to a proper value by the addition of a small quantity of acid, base or buffer salt.

When the goods and dyestuff are added to the dye bath with the latter at a relatively low temperature, it is generally necessary to thereafter increase the temperature of

the bath in order to obtain a satisfactory degree of exhaustion. The rate at which the temperature of the dye bath is increased can vary from an exceedingly low value, as illustrated by 0.1° F. per minute, up to the limits of the apparatus employed or in other words up to about 10° F. per minute. Conventional rates of temperature increase give excellent results and as a general rule a rate of temperature rise of from about 2 to 5° F. per minute is preferred. Raising the temperature of the bath can be commenced immediately after adding the dyestuff, if desired, although an alternative procedure which is advantageous in some instances comprises retaining the dye bath at a constant temperature for from about 5 to 10 minutes to allow completion of the initial dye strike.

The ultimate temperature of the bath may be conventional and most milling colors are conventionally dyed at the boil. If, however, there is danger of damage to the fabric or if a low terminal temperature is advantageous for other reasons, reasonably satisfactory results can generally be achieved by employing a terminal temperature of only about 180° F. Likewise, one can employ pressure equipment and raise the temperature of the bath above the boiling point, although such a procedure is seldom, if ever advantageous.

As the dyeing progresses, it is generally advantageous to gradually reduce the pH of the dye bath to thereby hasten the exhaustion of the dye and to result in a more complete exhaustion of the dye onto the fabric or the like. This invention results in the dye bath pH being less critical than in prior art procedures using the milling colors but, for best results, the pH of the bath should be reduced as evenly and uniformly as possible and sudden changes in pH should be avoided. For this reason, the use of an ammonium or other heat decomposable salt is generally advantageous as it permits an exceedingly uniform reduction in the pH of the bath, and eliminates the sudden pH changes which are inherent in the alternative procedure of adding small quantities of dilute acid as the dyeing progresses. In some instances it is advantageous to resort to the use of a decomposable salt in combination with acid additions and this is particularly true when one desires a terminal pH which is slightly lower than can be readily achieved with ammonium salts. By such a combination of reagents the pH of the bath can be controlled during the early part of the dye cycle by the ammonium salt, and near the termination of the dyeing, the pH can be lowered by dilute acid additions to achieve a more nearly complete exhaustion of the dye. The amount of acid forming salt and/or free acid that is added to the dye bath is determined entirely by the necessary requirements for reducing the pH of the bath to a suitable terminal value and this amount will vary depending upon the amount of dyestuff, guanidine compound and other reagents employed in the dye bath as well as the terminal pH necessary for a reasonably complete exhaustion of the dyestuff. From about 2 to 5%, based on the weight of goods, of the acid forming salt is generally sufficient to result in a satisfactory terminal pH without resorting to acid additions and it is seldom advantageous to use more than about 10 to 15% of the salt. If too little is employed and the exhaustion of the dye bath is not reasonably complete, it is usually possible to add a small amount of acid to drop the pH to a suitable terminal value. Examples of suitable acid producing salts which may be employed in the process are ammonium acetate, ammonium sulfate and diammonium phosphate. Examples of suitable acids which may be employed include acetic acid and propionic acid. Inorganic acids such as hydrochloric or sulfuric acid can be employed but are generally not advantageous because of the small changes in pH which are desired.

The most advantageous terminal pH for the dye bath depends entirely upon the nature of the dye employed and the terminal pH is preferably that which will just result in a reasonably complete exhaustion of the dye

onto the fabric. Many milling colors will exhaust to a reasonably complete degree at a pH of 6 or higher and in some instances the terminal pH may be as high as 7.5. On the other hand, some milling colors require a terminal pH of about 5 for a satisfactory degree of exhaustion. The terminal pH of the dye bath is not extremely critical as long as the degree of exhaustion is satisfactory and good results can generally be achieved utilizing a terminal pH of 5 even with a dye that completely exhausts at a pH of 6 so that, if desired, one can simply reduce the pH of the bath to about 5 regardless of the dyestuff employed.

The length of time required for reasonably complete exhaustion of the dye bath is determined primarily by the rate at which the pH of the bath is reduced. As a general rule, the slower the rate of exhaustion, the more level the dyeing but a very level color can generally be obtained by controlling the rate of exhaustion such that the bath is at its terminal temperature for from about 30 minutes to one hour. If one is employing an acid liberating salt, the rate of exhaustion can be controlled by varying the amount of the salt used and by the selection of a salt having the particular characteristics desired. If the pH is being partially or totally controlled by acid additions, the rate of exhaustion can be controlled by the frequency of addition and the quantity of acid added.

The invention will now be illustrated by the following specific examples in which all parts are by weight unless otherwise indicated:

Example I

Into a dye beck there is loaded 110 pounds of a chlorinated woolen material containing 12½% nylon, and approximately 950 gallons of water at a temperature of about 80° F. There is then slowly added to the beck 0.55 pound of sym.-diphenylguanidine dissolved in 2.75 pounds of sulfonated castor oil (Monipol Oil 48) and 1.1 pounds of an alkylaryl polyether sulfate dispersing agent sold under the trade name of Triton 770. Diphenylguanidine is only slightly soluble in water and the addition of the dispersing agent solution results in a fine dispersion of the guanidine compound in the bath. The pH of the bath at this time is approximately 7.6. After about 10 minutes and with the dye bath still at a temperature of about 80° F., there is added 0.092 pound of Brilliant Indocyanine GA-CF (PR. 223) dissolved in about 4 gallons of water. The temperature of the dye bath is then slowly raised to the boil over a period of one hour and the pH at the boil is found to be approximately 7.85. After 40 minutes at the boil the steam is cut and 0.55 pound of acetic acid are added very slowly. The dye bath is then retained at the boil for an additional 20 minutes at the end of which time the degree of exhaustion is satisfactory. The pH of the dye bath at this time is about 5.2. The dye bath is dropped, and the goods rinsed and dried. The finished goods have an excellent hand and are found to have been dyed a very level and bright aqua blue.

Example II

Into a dye beck there is loaded 140 pounds of a woolen fabric and approximately 1,000 gallons of water at a temperature of approximately 75° F. There is then added to the bath approximately 4.2 pounds of ammonium acetate and 0.56 pound of sym.-diphenylguanidine dissolved in 3.5 pounds of sulfonated castor oil and 1.4 pounds of an alkylaryl polyglycol non-ionic dispersing agent sold under the trade name of Tergitol NPX. The pH of the bath at this time is approximately 7.5. After approximately 10 minutes there is added to the bath a dye mixture comprising 3.85 pounds of Polar Brown 2GL (Geigy Chemical Corporation), 0.14 pound of Erie Scarlet B (CI 382) and 0.112 pound of Alizarine Cyanine Green G (CI 1078) and the temperature of the dye bath is thereafter raised to the boil over a period of approximately one hour. After approximately 45

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minutes at the boil the degree of exhaustion is satisfactory and the pH is found to be approximately 6.0. The dye bath is dropped and the goods are rinsed and dried. The finished goods are found to have an excellent hand and are dyed a level brown color.

Example III

Into suitable dyeing apparatus there is loaded 80 parts by weight of a woolen fabric and 3,200 parts by weight of water at a temperature of approximately 80° F. There is then added to the bath 2 parts by weight of diammonium phosphate and 0.4 part by weight of sym-tetramethylguanidine dissolved in 2.5 parts of a sodium alkyl sulfate wetting agent sold under the trade name of Tergitol Anionic 4. After a period of approximately 15 minutes with the dye bath still at a temperature of about 80° F., there is added a dye mixture comprising 0.335 part of Benzyl Fast Orange G (Ciba), 0.48 part of Benzyl Fast Yellow G (Ciba) and 2.0 parts of Erio Fast Cyanine Green G (CI 1078). The dye bath is raised to the boil over a period of approximately 45 minutes and retained at the boil for approximately one hour after which the bath is dropped and the goods rinsed. The finished goods have an excellent hand and are dyed a level green.

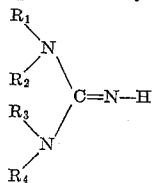
Example IV

Into a suitable dye apparatus there is loaded 90 parts by weight of a woolen fabric and approximately 350 parts by weight of water at a temperature of about 80° F. There is then added to the bath 2.7 parts of ammonium sulfate and 0.25 part of sym-dibenzylguanidine dissolved in 2.3 parts of sulfonated castor oil and one part of an alkylarylpolyether sulfate wetting agent sold under the trade name of Triton 770. After a period of about 10 minutes there is added a dye mixture comprising 0.135 part of Alizarine Cyanine Green G (CI 1078), 1.12 parts of Polar Brilliant Violet BL (Geigy) and 0.18 part of Anthraquinone Violet D (CI 1080). The temperature of the dye bath is then raised to the boil over a period of about 50 minutes and after about 30 minutes at the boil there is slowly added 0.4 part of acetic acid. The dye bath is retained at the boil for an additional 15 minutes and then dropped. The finished goods have an excellent hand and are dyed a level lavender shade.

The procedure for employing other guanidine compounds and other dyestuffs is the same as illustrated in the above examples.

Having thus described my invention what I desire to claim and secure by Letters Patent is:

1. In a process for dyeing with high affinity milling colors textile fibers selected from the group consisting of nylon and proteinaceous fibers, the improvement which comprises adding to the bath in which the fibers are dyed a guanidine compound selected from the group consisting of bases represented by the formula:



wherein R_1 , R_2 and R_3 represent members selected from the group consisting of hydrogen, monocyclic aromatic radicals, aliphatic radicals, and cycloalkyl radicals, and R_4 represents a radical selected from the group consisting of monocyclic aromatic, aliphatic and cycloalkyl radicals; and acid addition salts thereof.

2. The improvement of claim 1 wherein the guanidine compound is sym.-diphenylguanidine.

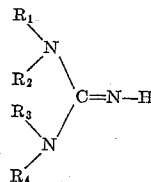
3. The improvement of claim 1 wherein the guanidine compound is employed in amounts of from about 0.1% to 15% based upon the weight of goods to be dyed.

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4. The improvement of claim 1 wherein the guanidine compound is added to the dye bath in the form of solution in an organic solvent comprising a dispersing agent.

5. The improvement of claim 4 wherein the dispersing agent comprises sulfonated castor oil.

6. A process for dyeing with high affinity milling colors textile fibers selected from the group consisting of nylon and proteinaceous fibers, which process comprises placing the goods to be dyed in an aqueous bath, dispersing in said bath, prior to the addition of dyestuff, a guanidine compound selected from the group consisting of bases represented by the formula:



wherein R_1 , R_2 and R_3 represent members selected from the group consisting of hydrogen, monocyclic aromatic radicals, aliphatic radicals, and cycloalkyl radicals, and R_4 represents a radical selected from the group consisting of monocyclic aromatic, aliphatic and cycloalkyl radicals; and acid addition salts thereof, adjusting the pH of the bath to a value of at least about 7 but not sufficiently high to result in damage to the goods, adding a dyestuff solution containing at least one milling dye and thereafter heating the dye bath to result in the dye being exhausted onto said goods.

7. A process according to claim 6 wherein the guanidine compound and dyestuff are added at a temperature below about 110° F. and the dye bath is thereafter heated to a temperature of at least about 180° F.

8. A process according to claim 7 wherein the pH of the bath is reduced during the dyeing to a terminal value of no more than about 6.

9. A process according to claim 8 wherein the pH is reduced by the procedure which comprises adding to the dye bath an ammonium salt which decomposes under the influence of heat to liberate an acid.

10. A process according to claim 9 wherein the ammonium salt is ammonium acetate.

11. A process according to claim 8 wherein the guanidine compound is added to the dye bath in the form of a solution in a dispersing agent.

12. A process according to claim 11 wherein the dispersing agent comprises sulfonated castor oil.

13. A process according to claim 6 wherein the guanidine compound is a diarylguanidine base.

14. A process according to claim 13 wherein said guanidine base is sym.-diphenylguanidine.

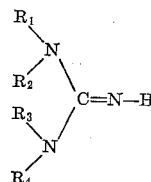
15. A process according to claim 6 wherein the guanidine compound is a diaralkylguanidine base.

16. A process according to claim 15 wherein the guanidine base is sym.-dibenzylguanidine.

17. A process according to claim 6 wherein the guanidine compound is an alkylguanidine.

18. A process according to claim 17 wherein the guanidine base is sym.-tetramethylguanidine.

19. A process for dyeing proteinaceous materials with high affinity milling colors which process comprises placing the material to be dyed in an aqueous bath, dispersing in said bath a guanidine compound selected from the group consisting of bases represented by the formula:



wherein R₁, R₂ and R₃ represent members selected from the group consisting of hydrogen, monocyclic aromatic radicals, aliphatic radicals, and cycloalkyl radicals, and R₄ represents a radical selected from the group consisting of monocyclic aromatic, aliphatic and cycloalkyl radicals; and acid addition salts thereof, adjusting the pH of said bath to a value of from about 7 to 8, adding the milling color dyestuff while the temperature of the bath is not higher than about 110° F., raising the temperature of the bath to at least about 180° F. and gradually reducing the pH of the bath to a value of from about 5 to 6.

20. A process according to claim 19 wherein the material to be dyed is a chlorinated woolen fabric and the guanidine compound is sym.-diphenylguanidine.

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