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INHIBITING THE GAS FADING OF DYED
ACETATE SILK

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This invention relates to improvements in dyed cellulose acetate fibers, and especially to the prevention of fading which results when such dyed fibers are exposed to deleterious fumes, such as atmosphere which contains oxides of nitrogen or sulfur.

When dyed articles of cellulose acetate fibers are stored where they are exposed to atmosphere containing oxides of nitrogen and sulfur it has been observed that the dyeings change shade and lose strength. Fading is produced more or less rapidly by the action of various concentrations of the deleterious gases. Even in minute concentration, the deleterious gases are effective, as for example where the dyed goods are stored or exposed for a considerable period of time to an atmosphere which contains such small amounts of the deleterious oxides. It is therefore desirable to provide dyed cellulose acetate fibers so that they will have good fastness to dry cleaning and washing and will resist the action of deleterious gases. Means for such purposes are desired which will not have a harmful effect on the shade or fastness properties of the dyes.

It is among the objects of the invention to provide means to inhibit the action of such deleterious gases on dyed cellulose acetate fibers. Another object of the invention is to provide inhibitors which do not deleteriously affect the shade and fastness of the dyes and which will give effective protection after the goods are cleaned. Other objects of the invention will be apparent from the following description.

The objects of the invention are attained in general by affixing to the fibers certain biguanides. These may be conveniently applied or affixed to the fibers by wetting or saturating the dyed fibers with a water solution or suspension of the inhibitor and then removing the water.

The invention will be more fully set forth in the following more detailed description which includes examples that are given as illustrative embodiments of the invention and not as limitations thereof. Parts are expressed in parts by weight unless otherwise noted.

Example I

One-half to two parts of phenyl biguanide were dissolved in 100 parts of water by gentle warming and stirring. Five parts of cellulose acetate silk which had been dyed with 1,4-di(mono methyl amino) anthraquinone were immersed for a period of from 30 seconds to three minutes in the solution of phenyl biguanide. The solution temperature was between 25° and 100° C. The acetate rayon was removed and dried.

On exposure to the fumes of a gas burner and to atmosphere containing oxides of nitrogen, the

dyeing was unchanged after a period of time in which an untreated dyeing of the same kind faded to a pink shade. After several dry-cleanings with an organic solvent, the treated dyeing retained most of the protection against the gas fumes. The treatment was found to improve the light fastness of the dyeing.

The phenyl biguanide solution could be used repeatedly or until it was exhausted of the inhibiting agent to a considerable extent.

When the dyed cellulose acetate silk was similarly treated with ortho tolyl biguanide, like results were produced.

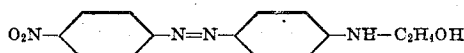
Example II

One part of phenyl biguanide was intimately mixed into a water solution containing one-half part of soap. Five parts of cellulose acetate silk dyed with 1,4,5,8-tetra-amino anthraquinone were entered and saturated in the dispersion which was held at 70° C. After five minutes, the saturated material was removed, rinsed and dried. Upon exposure to an atmosphere containing oxides of nitrogen, it remained unchanged while an untreated dyeing of the same kind faded to a considerable extent.

Similar results were obtained by using phenyl, ethyl biguanide in suspension instead of phenyl biguanide.

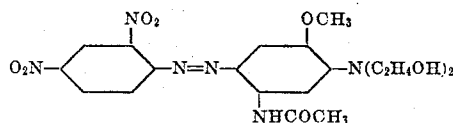
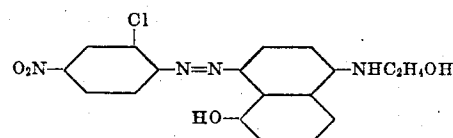
Example III

Cellulose acetate fabrics dyed with the azo dye represented by the formula



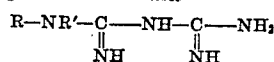
were severally treated with phenyl biguanide and ortho tolyl biguanide similarly to the treatment described in Example I and similar protection from gases containing oxides of nitrogen and sulfur was obtained.

These treatments gave good protection to dyeings on acetate silk which were dyed with the following compounds:

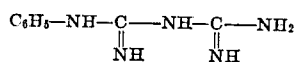


A large number of biguanides can be used in accordance with the invention and with the effect described in the foregoing examples. Such

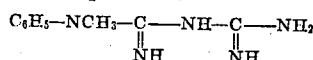
biguanides, sometimes called biguanidines or guanyl guanidines may be readily prepared by reacting a primary or secondary amine with dicyan diamide in the manner described in Jour. ft., prakt. Chem., 84, 396, thereby producing biguanides of the general formula



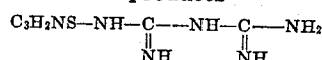
wherein R' is hydrogen or the substituted group of the secondary amine. Mono-, bis- or trisbiguanides are produced when one, two or three groups are present in the nucleus. Accordingly aniline produces



N-methyl aniline produces

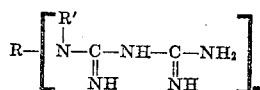


and 2-amino thiazole produces



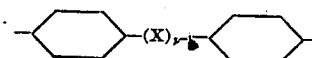
all of which have the described effect of the biguanides mentioned in the foregoing examples. As illustrative of the class of biguanides which are useful for the purposes of the present invention and which may be produced in like manner from arylamines and heterocyclic amines, the following amines are mentioned as the starting materials from which such representative biguanides are made; aniline, o, m and p-toluidines, xylydines, cresidine, 2,5-dimethoxy aniline, mono- and di-chlor anilines, o, m and p-cyano aniline, m-amino benzotrifluoride, o, m and p-amino phenyl methyl sulfone, o, m and p amino acetophenone, p-amino phenyl beta-hydroxy ethyl ether, o, m and p-anisidine and phenetidine, p-dodecyl aniline, p-amino ethyl benzoate, sulfanilamide, p-amino acetanilide, o, m and p-phenylene diamine, m-toluene diamine, 2,4-diamino anisol, 2,4-diamino chlorbenzene, benzidine, toluidine dianisidine, 2,4,4'-triamino diphenyl, 1,3,5-triamino benzene, 2,4,6-triamino toluene, 4,4'-diamino diphenyl ether, thioaniline, 4,4'-diamino diphenyl sulfone, 4,4'-diamino diphenyl urea, p-amino benzoyl m-phenylene diamine, m-amino benzoyl p-phenylene diamine, m-amino benzene sulfonyl m-phenylene diamine, 4,4'-diamino stilbene, 1,2-di(4,4'-amino-phenoxy) ethane, 1,2-di(3-amino phenyl) ethane, 4,4'-diamino diphenyl amine, 4,4'-diamino diphenyl methane, 4,4'-di(mono ethyl amino) diphenyl methane, m-amino phenyl methyl pyrazolone, 2-amino-4-methyl thiazol, 2-amino benzothiazol, amino tetrazol, 2- and 3-amino pyridine, 2,6-diamino pyridine, 2,4,6-triamino pyridine, alpha and beta-naphthylamine, 2-methoxy-1-naphthylamine, 4-amino N-methyl naphtho styryl, amino antipyrène, N-methyl aniline, N-ethyl aniline, N-hydroxy ethyl aniline, N-butyl aniline, N-methyl o-toluidine, n-methyl aniline, hydroxy propyl aniline, hydroxy amyl aniline, 2-hydroxy-3-chlor-propyl aniline, 4-amino-diphenyl sulfone and 4-amino diphenyl.

Accordingly, the compounds useful as inhibitors are the mono-, bis- and trisbiguanides which may be represented by the formula

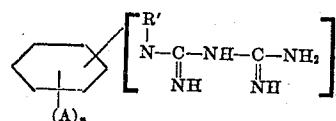


in which the nuclear radical R is from the ben-

zene, naphthalene or heterocyclic series and the series of diphenyl compounds represented by the formula



in which X is one of a group consisting of $-\text{O}-$, $-\text{S}-$, $-\text{NH}-$, $-\text{CH}_2\text{SO}_2-$, $-\text{CO}-$, $-\text{CH}_2\text{CH}_2-$, $-\text{CH}=\text{CH}-$, $-\text{NHCO}-$, $-\text{NHCONH}-$, $-\text{OCH}_2\text{CH}_2\text{O}-$, and $-\text{NHSO}_2-$; and p is an integer not greater than 2. In cases where p is 1, the radical has no bridging group. Any of these nuclei may be unsubstituted or substituted once to twice by any combination of alkyl groups having 1 to 12 carbons, methoxy, ethoxy, CF_3 , halogen, $-\text{COCH}_3$, CN, acetyl amino, $-\text{SO}_2\text{CH}_3$ and $-\text{SO}_2$ phenyl. The diphenyl compounds can be substituted in each benzene ring. In the above formula m is 1 to 3 and R' is one of a group consisting of hydrogen, alkyl having 1 to 5 carbons and hydroxyalkyl having 1 to 5 carbons. The biguanides of the benzene series are the preferred embodiments, such as those represented by the formula



wherein A represents the nuclear substituents heretofore recited and n is 1 or 2, and of these the mono-biguanides are preferred.

The biguanides used in carrying out the invention have good affinity for cellulose acetate fibers resulting in rapid absorption and good retention by the fiber, but the precise reasons for their inhibiting action are not fully understood. It has been suggested that the inhibiting effect may be due to the formation of salts or oxides by the action of the deleterious fumes on the biguanides in preference to a salt forming or oxidizing action on the dye. The nature of the reaction products is not fully known and it is to be understood that the invention is not limited by the proposed theory.

The invention is especially useful in improving the properties of dyed cellulose acetate fibers which are dyed with the anthraquinone and the monazo dyes, such as 1,4 di(mono hydroxy ethyl amino) anthraquinone, 1-methyl amino-4-hydroxy ethyl amino anthraquinone, 1-amino-4-methyl amino anthraquinone, 1,4-diamino-5-nitro anthraquinone, 1-amino-4-anilidoanthraquinone and 4-amino-4'-nitro-azobenzene with which a similar degree of protection is afforded by the biguanides described.

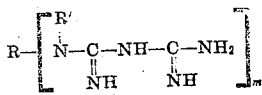
It is commonly preferable to apply the biguanides as an after treatment to the dyed fiber but it may be applied during the dyeing operation by adding the inhibiting compound to the dyebath or other treating bath. Any manner of affixing or adsorbing the inhibitor on and in the fiber gives beneficial results. A short immersion of the fibers, such as about thirty seconds is frequently sufficient to give adequate protection but better results are sometimes obtained with longer immersions, such as three to five minutes. The adsorption of the inhibitor varies somewhat with the various circumstances but it is generally quite rapid. Considerably longer immersions than those mentioned can be employed when they are desired since they are not harmful, but such excessively long immersions are commonly unnecessary. The best duration

of time for immersing the fibers may vary somewhat depending on circumstances, such as the particular inhibitor used, the character and condition of the fiber and the temperature and character of the treating bath. The wide variation permissible in the treatment is advantageous since it lends itself desirably to the special circumstances encountered in practice. The fastness of the dyeings is not adversely affected and in most cases it is improved.

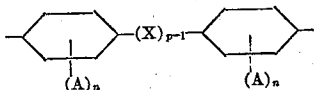
From the foregoing disclosure it will be recognized that the invention is susceptible of modification without departing from the spirit and scope thereof and it is to be understood that the invention is not restricted to the specific illustrations herein set forth.

We claim:

1. A dyed article of cellulose acetate fibers which has affixed to said fibers a biguanide of a group represented by the formula



in which R is a nucleus of the benzene, naphthalene heterocyclic and

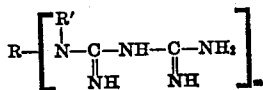


series, m is 1 to 3; R' is one of a group consisting of hydrogen, alkyl having 1 to 5 carbons and hydroxyalkyl having 1 to 5 carbons; A is from the group consisting of hydrogen, alkyl having 1 to 12 carbons, methoxy, ethoxy, $-\text{CF}_3$, halogen, $-\text{COCH}_3$, $-\text{CN}$, acetyl amino, $-\text{SO}_2\text{CH}_3$ and $-\text{SO}_2$ phenyl; n is an integer not greater than 2; X is one of a group consisting of $-\text{O}-$, $-\text{S}-$, $-\text{NH}-$, $-\text{CH}_2\text{SO}_2-$, $-\text{CO}-$, $-\text{CH}_2\text{CH}_2-$, $-\text{CH}=\text{CH}-$, $-\text{NHCO}-$, $-\text{OCH}_2\text{CH}_2\text{O}-$ and $-\text{NHSO}_2-$; and p is an integer not greater than 2.

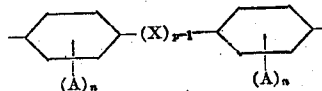
2. A dyed article of cellulose acetate fibers which has affixed to said fibers phenyl biguanide.

3. A dyed article of cellulose acetate fibers which has affixed to said fibers phenyl ethyl biguanide.

4. In the process of inhibiting the action of gases which are deleterious to dyeings on cellulose acetate fibers, the steps which comprise wetting the dyed fibers with an aqueous fluid containing a biguanide and then removing the water so as to affix the biguanide to the fibers, said biguanide being represented by the formula

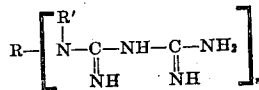


in which R is a nucleus of the benzene, naphthalene, heterocyclic and

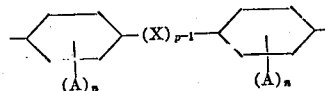


series, m is 1 to 3; R' is one of a group consisting of hydrogen, alkyl having 1 to 5 carbons, hydroxyalkyl having 1 to 5 carbons; A is from the group consisting of hydrogen, alkyl having 1 to 12 carbons, methoxy, ethoxy, $-\text{CF}_3$, halogen, $-\text{COOCH}_3$, $-\text{CN}$, acetyl amino, $-\text{SO}_2\text{CH}_3$ and $-\text{SO}_2$ phenyl; n is an integer not greater than 2; X is one of a group consisting of $-\text{O}-$, $-\text{S}-$, $-\text{NH}-$, $-\text{CH}_2\text{SO}_2-$, $-\text{CO}-$, $-\text{CH}_2\text{CH}_2-$, $-\text{CH}=\text{CH}-$, $-\text{NHCO}-$, $-\text{NHCONH}-$, $-\text{OCH}_2\text{CH}_2\text{O}-$, and $-\text{NHSO}_2-$; and p is an integer not greater than 2.

5. In the process of inhibiting the action of gases which are deleterious to dyeings on cellulose acetate fibers, the steps which comprise saturating the dyed fibers with an aqueous fluid containing a biguanide and then removing the water so as to affix the biguanide to the fibers, said biguanide being represented by the formula



in which R is a nucleus of the benzene, naphthalene, heterocyclic and



series, m is 1 to 3; R' is one of a group consisting of hydrogen, alkyl having 1 to 5 carbons, hydroxyalkyl having 1 to 5 carbons; A is from the group consisting of hydrogen, alkyl having 1 to 12 carbons, methoxy, ethoxy, $-\text{CF}_3$, halogen, $-\text{COOCH}_3$, $-\text{CN}$, acetyl amino, $-\text{SO}_2\text{CH}_3$ and $-\text{SO}_2$ phenyl; n is an integer not greater than 2; X is one of a group consisting of $-\text{O}-$, $-\text{S}-$, $-\text{NH}-$, $-\text{CH}_2\text{SO}_2-$, $-\text{CO}-$, $-\text{CH}_2\text{CH}_2-$, $-\text{CH}=\text{CH}-$, $-\text{NHCO}-$, $-\text{NHCONH}-$, $-\text{OCH}_2\text{CH}_2\text{O}-$ and $-\text{NHSO}_2-$; and p is an integer not greater than 2.

6. In the process of inhibiting the action of gases which are deleterious to dyeings on cellulose acetate fibers, the steps which comprise wetting the fibers with an aqueous fluid containing phenyl biguanide and then removing the water, thereby to affix said biguanide to the fibers.

7. In the process of inhibiting the action of gases which are deleterious to dyeings on cellulose acetate fibers, the steps which comprise wetting the fibers with an aqueous fluid containing phenyl ethyl biguanide.

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