

UNITED STATES PATENT OFFICE

2,261,294

PROCESS OF INCREASING THE AFFINITY
OF FIBERS AND FILMS FOR ACID AND
SUBSTANTIVE DYESTUFFSPaul Schlack, Berlin-Treptow, Germany, assign-
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Duisberg, New York, N. Y.No Drawing. Application July 10, 1937, Serial No.
152,994. In Germany July 24, 1936

5 Claims. (Cl. 8-113)

My present invention relates to a process of improving the dyeing properties of natural or artificial fibrous material and foils and more particularly to a process in which fibrous materials or foils containing acid hydroxyl-groups are treated with alkylene imines or their salts.

It is an object of the invention to provide a process by which the affinity of these products towards acid and substantive dyes is essentially increased.

Further objects will be apparent from the detailed specification following hereafter.

My invention is based on the observation that natural products or artificial structures such as fibers, sheets, leather, wood or paper which contain in a fixed form residues with hydroxyl groups united with carbon and of pronounced acid character, especially carboxyl groups or mercapto alkyl groups but not when united to protein residues, acquire an intense affinity for dyestuffs of all kinds having acid groups if they are subjected, if desired during or immediately following the shaping operation, to a treatment with an alkylene imine or a salt thereof. In this manner the original affinity of the structure for basic dyestuffs decreases as the action of the alkylene imine increases and may finally completely disappear. If the goods under treatment are very rich in acid groups at intermediate stages of the treatment the affinity for acid or basic dyestuffs may suffice but in the case of basic dyestuffs it is advantageous to dye at comparatively low temperatures.

The process based on the foregoing observation is especially important in cases in which the difficulties of dyeing are greatest, namely in particular the dyeing of artificial structures, especially fibers or products made therefrom, which consist or did consist originally essentially of organophil components, for example structures of organic cellulose derivatives such as acetyl cellulose or ethyl cellulose; also structures from vinyl polymerides, for instance polyvinyl esters, polyvinyl acetals, polyvinylacetal-acid esters and such mixed polymerizates as contain vinyl esters, acrylic acid esters, acrylic acid amides, acrylic acid nitriles as components. In so far as the structures contain saponifiable groups, they may be pretreated with a saponifying agent or denitrating agent before being subjected to the action of the alkylene imine whereby the reactivity is increased. Such a saponification may be conducted in a manner in itself known, such that it follows a heterogeneous course, that is to say there is a stratified action or that it is compara-

tively uniform, occurring also in the deeper layers, the action thus being quasi-homogeneous or permutoid. In general the last named type of reaction which is obtainable with ammonia or organic amines has the advantage. By such a saponification the acid groups necessary for the process, in particular the carboxyl groups, are first unblocked. Obviously also free phenolic hydroxyl groups may be produced in this manner, but generally speaking phenol esters are so freely capable of hydrolysis that their scission occurs already by the action of the imine in case they are used in the form of the free base. It is therefore not unconditionally necessary in such cases that there should be a separate preliminary saponification treatment. Reactive carboxyl groups can also be produced from suitable components by means of a pretreatment with an oxidizing agent correspondingly with the disclosure contained in U. S. patent application Ser. No. 57,524, filed January 4, 1936.

For the process of this invention there are used acid components which are named in large number in the aforesaid U. S. patent application Ser. No. 57,524. Here, therefore, only the more important components will be named, polymeric carboxylic acids, their anhydrides and esters, in particular mixed polymerizates obtained from unsaturated mono- or di-carboxylic acids and functional derivatives thereof as components, for example mixed polymerizates from vinyl alkyl ethers and maleic acid anhydride, mixed polymerizates from acrylic acids and acrylic acid esters, acrylic acid nitriles or acrylic acid amides, ester acids of cellulose, especially such as are derived from organic cellulose derivatives which still contain hydroxyl groups; esters of pectin, alkyl resins having a high acid number, anhydric condensation products from aromatic hydrocarbons with side chains carrying hydrogen in α -position and α - β -unsaturated dicarboxylic acid anhydrides (U. S. patent application Ser. No. 733,126, now Patent No. 2,121,183) for instance a product of the reaction of xylene and maleic acid anhydride, also phenol aldehyde resins and their acyl derivatives, especially acetyl derivatives, acetyl tannin, sulfur products from phenol of high molecular weight, polyvalent mercapto compounds and acyl derivatives thereof, for instance the acylated reaction product of the chlorinated resin from xylene formaldehyde with potassium hydrosulfide.

It is to be noted that the process is in no way limited to the above mentioned products from organophil highly polymeric bodies. It is equally applicable to structures of the more or less pro-

nounced hydrophil substances, for example natural or artificial cellulose products like cotton, cellulose artificial fibers with which the acid components, for instance pectin substances, polyacrylic acids, mixed polymerizates from maleic acid and vinylalkyl ether, vinyl ester or vinyl halide, phenol aldehyde resins, phenol aldehyde resins which have been caused to react with chloroacetic acid, tannin, sulfurized phenols have been incorporated before or during the spinning or casting process. The incorporated substance must, so as to be within the scope of the invention, be fixed in the structure and therefore must be with difficulty or not at all removable by water. A simple impregnation with a water-soluble body of low molecular weight which has no affinity for the fiber, that is to say which is not fixed or precipitated on the fiber, is not within the ambit of this invention.

A particularly strong action is produced when the acid groups, particularly carboxylic acid groups, have been saturated with organic bases before the reaction with alkylene imine, the organic bases carrying halogen alkyl groups, preferably several; such as three or more. Not only are nitrogen bases useful for this purpose, but also bases containing 5-valent phosphorus or 4-valent sulfur as a basic element. Suitable bases are, for instance, the chloro- and bromo-alkylamines obtainable by halogenation of oxalkyl bases, for instance $\beta\beta'$ -dichlorodiethylamine, $\beta\beta'\beta''$ -trichloroethylamine, the products of the action of excess of alkylene halide such as ethylene chloride, ethylene bromide, trimethylene bromide or 1:2:3-trichloropropane on mono- and polyamines such as triethylamine, ethylene diamine or tetramethylethylene diamine. Especially suitable for use are the poly- γ -chloro- β -hydroxy-propylamines obtainable in completely colorless condition, which are accessible in good yield by the invention of U. S. patent application Serial No. 53,003, filed December 5, 1935, now Patent No. 2,143,383, from ammonium salts or amine salts.

A reinforcing effect is produced by a pretreatment with a polyvalent mercapto alkylamine, for instance the reaction product of ethylene diamine and 4 mols propylene sulfide. The mercaptans are preferably applied to the structure in presence of a reducing agent, for instance a hydro-sulfite, in order to prevent oxidation or premature oxidation.

As example of imines suitable for the invention the following may be named: ethylene imine, C-methyl-ethylene imine, N-methylethylene imine, N-butylethylene imine, N-cyclohexylethylene imine, the quaternary iminium salts from N'N'-dimethyl-N'N'-di- β -chloroethylethylene diamine and NN'-di- γ -chloro- β -hydroxypropyl piperazine. Quaternary iminium salts are advantageously used in the case of hydrophil structures, but in the case of hydrophobe fibers they generally give only comparatively feeble effects.

In so far as imines are sufficiently volatile the treatment may preferably be conducted in a gaseous phase, especially if hydrophobe structures are to be aminated. In the most favorable cases, that is to say, when very reactive products are being treated, reaction may occur at a suitable temperature as a continuous operation. Imines which are non-volatile or insufficiently volatile or salts of imines, for instance acetates, toluene sulfonates, dodecyl sulfonates, may be dissolved, for instance in water, alcohol or an inert organic

solvent or emulsified with one of these. Liquid imines, for example N-butylethylene imine as well as the higher homologues thereof, may be used directly by spraying them on the goods to be treated, especially if by subsequent raising of the temperature in a closed vessel there is produced at least a partial evaporation and thereby a uniform distribution of the agent. Such a spraying operation is particularly suitable when cut staple fibers are under treatment.

The reaction may be combined with an amination of groups with alkylating function attached to residues of high molecular weight. Components suitable for this special case are for instance those resins having alkylating groups named in U. S. patent application Serial No. 41,500, filed September 20, 1935, now Patent No. 2,142,007, and also cellulose derivatives having reactive halogen. An alkylene imine, for instance ethylene imine may be the sole reactive agent. However, with a special advantage may be used besides alkylene imines another aminating agent or its equivalent, for instance pyridine, trimethylamine, isoquinoline, or triethylene phosphine. Mixtures may also be used which contain, for example besides a free tertiary base such as pyridine, an ethylene imine in the form of a salt, for instance the acetate or paratoluene sulfonate. In this manner control of the action and an influence on its course in any particular direction is possible, since the acetate for instance of the imine does not in general react with a halogen alkyl group united to a high molecular residue in a non-salt-like manner. Obviously such reactions may be conducted in stages which may be of advantage when one desires first to satisfy the tendency of the acid groups to combine with the dyestuffs and only then to change the character of the affinity of the structure for dyes, in order, for example, to top dye with a certain basic dyestuff another fibrous material present in the mixed fabric or in order to permit a further dyeing with an acid dyestuff. The combined action of the alkylene imine on the acid groups and the amination of the groups with alkylating function is especially of interest in a case of fibers and other structures of hydrophobe character. As such may be cited fibers from acetyl cellulose which contain in addition to a mixed polymerizate having free carboxyl groups or carboxyl groups which spontaneously become free, for instance the mixed polymerizate from vinylmethyl ether and maleic acid anhydride, a highly polymeric substance with reactive halogen, bound in the manner of a hydrogen-halide-ester, for instance polyvinyl chloracetate.

The structures obtained or changed by the process of the invention may be dyed with very many acid and substantive dyestuffs of the various classes in various tints which have good properties of fastness. Structures which already exhibit affinity for the dyestuffs in question acquire an increased dyeing capacity, and in most cases the fastness of the dyeings is not inconsiderably increased. The fastness on cellulose fibers and fibers of cellulose derivatives may certainly in the most favorable cases exceed the fastness of analogous dyeings on wool. The structures exhibit an increased resistance towards the hydrolizing action of mineral acids.

A further improvement of the fastness of the dyeings may be achieved by treatment with an alkylating agent before, during or after the dyeing. Suitable alkylating agents are, for example,

dimethyl sulfate, para-toluene sulfonic acid methyl ester, epichlorhydrin, 3-chloro-1,2-propylene sulfide, chloroacetic acid diethylamide, benzyl chloride, xylene-bromide, 1,4-dichlorobutene-2,3, α,α -dichlorodimethyl-ether, chloracetone, 1:3-dichloroacetone, diethylethylene-iminiumchloride. In this connection reference may be made to my copending applications Ser. No. 53,004 filed December 5, 1935, now Patent No. 2,131,146; Serial No. 60,061 filed January 21, 1936, now Patent No. 2,131,121, and Ser. No. 123,868 filed February 3, 1937.

Also agents which convert the amino group into a guanidine group, for instance isothio urea ethers, cyanamide, alkyl sulfo-cyanides may be used in after-treatment (compare U. S. patent application Ser. No. 123,867, filed February 3, 1937). Both the primary treatment and the after-treatment may occur in the presence of swelling agents for the substratum.

The following examples illustrate the invention:

1. A fabric of acetate artificial silk consisting of 90 per cent acetyl cellulose with 54 per cent of bound acetic acid and 10 per cent of a mixed polymerizate from 1 mol vinyl-methyl ether and 1 mol maleic acid anhydride is thoroughly desized at 60-65° C. by means of a soap solution containing 5 grams per liter, then acidified with a dilute acetic acid, rinsed and heated for 14 hours at 80° C. in a closed vessel of 50 parts by volume capacity containing 20 per cent of N-butyl-ethylene imine absorbed in a clay plate, the relative moisture being 75 per cent of atmospheric moisture. Care is taken that the atmosphere within the vessel is continually in motion, for example by rhythmic variation of pressure as described in U. S. patent application Ser. No. 46,445, filed October 23, 1935. After this treatment the goods are acidified with a solution of acetic acid containing 2 grams per liter for ¼ hour at 60° C. and are finally soaped for a short time. The fabric may now be dyed with many acid dyestuffs, for example Orange II (Schultz Farbstofftabellen, 7th ed., vol. I, page 86), Alizarine Direct Blue A (Schultz Farbstofftabellen, 7th ed., vol. II, page 9), Alizarinecyanine Green G Extra (Schultz Farbstofftabellen, 7th ed., vol. I, page 532), deep tones being produced; for example a liquor containing 6 per cent of Orange II, 10 per cent of Glauber salt and 4 per cent of acetic acid is exhausted at 60-75° C.

2. The same acetate artificial silk as is used in Example 1 after having been acidified is treated in a liquor ratio of 1:20 with 20 per cent of tetra- γ -chloro- β -hydroxypropyl ammonium chloride and the equivalent quantity of sodium acetate for 1 hour at 70° C. The silk remains pure white. It is then heated at 70° C. for 4 to 8 hours with 10 per cent of ethylene imine in the vapor phase, the volume ratio being 1:40 calculated on the weight of the goods. After acidifying the treated silk exhibits a strong affinity for substantive dyestuffs and quite especially for acid wool dyestuffs of the various classes. For example it can be dyed in very fast tints by after-chroming dyestuffs. Thus a 3 per cent dyeing with Acid Anthracene Brown KE (Schultz Farbstofftabellen, 7th ed., vol. II, page 187) becomes when after-chromed very fast to washing and fulling. The liquor and white material are only slightly tinted during alkaline fulling.

3. Acetate cellulose of the same constitution as given in Example 1 for the artificial silk there

prescribed is treated with 20 per cent of C-methyl-ethylene imine in the absence of a conditioning agent for 8 hours at 75° C.; the imine disappears completely. The thoroughly acidified fiber may be dyed with many acid dyestuffs, for example with Supranol Brilliant Red B (Schultz Farbstofftabellen, 7th ed., vol. II, page 204), Azo Acid Black 3 BL (Schultz Farbstofftabellen, 7th ed., vol. II, page 29), Alizarinecyanine Green G Extra; deep tints are produced.

4. Acetate artificial silk from acetyl cellulose containing 53 per cent of bound acetic acid and containing 12.5 per cent of the resinous anhydride made as described in U. S. patent application Ser. No. 733,126, now Patent No. 2,121,183, from xylene and maleic acid anhydride is heated with 15 per cent of ethylene imine in the vapor phase for four hours at 60° C. The fiber has now a distinct affinity for acid dyestuffs, for instance Orange II or Alizarine Direct Blue A.

5. The acetate artificial silk obtained by the dry-spinning process from a solution in methylene chloride and alcohol and having 58 per cent of bound acetic acid and 10 per cent of the acetyl tannin known in commerce under the trade mark "Tannigen" is treated with 15 per cent of ethylene imine for 14 hours at 80° C. in the gaseous phase. The silk can now be dyed with many acid dyestuffs, for instance Alizarine Direct Blue A.

6. To a crude solution of cellulose triacetate in acetic acid there are added 10 per cent of the mixed polymerizate from 1 mol maleic acid anhydride and 1 mol vinyl-methyl ether. The films made from this solution are easily dyed with basic dyestuffs and acquire affinity for acid dyestuffs when they are heated in a closed vessel at 80° C. with 15 per cent of ethylene imine for 16 hours or over-night. The period of the reaction may be essentially diminished by exposing the film to the action of the imine in a swollen condition. A suitable swelling agent is dioxane.

7. Acetate artificial silk having 54 per cent of bound acetic acid and containing 7.5 per cent of polyvinylchloracetate and 5 per cent of the mixed polymerizate from 1 mol maleic acid anhydride and 1 mol vinylmethyl ether is heated for 8 hours at 75° C. with the equivalent quantity of N-methylethylene imine calculated on the reactive chlorine and the unblocked carboxyl groups. The aminated and subsequently scoured artificial silk may be dyed in intense and fast tints by very many acid dyestuffs, especially dyestuffs capable of being chromed, and in many substantive dyestuffs, for example Crysophenene G (Schultz Farbstofftabellen, 7th ed. vol. I, page 295), Benzo Fast Scarlet 4 BS (Schultz Farbstofftabellen, 7th ed., vol. I, page 134), Diamine Pure Blue FF (Schultz Farbstofftabellen, 7th ed., vol. I, page 209), Sirius Light Blue F 3 GL (Schultz Farbstofftabellen, 7th ed., Suppl. vol., page 131), the dye bath containing 9 per cent of calcined Glauber salt and 4 per cent of acetic acid may easily be exhausted.

8. An acetate artificial silk made from an acetyl cellulose and in 54 per cent of bound acetic acid and containing 12 per cent of the mixed polymerizate from 1 mol maleic acid anhydride and 1 mol vinylmethyl ether is thoroughly soaped at 65° C. and soured with hydrochloric acid of 0.3 per cent strength; it is then immersed over-night (14 hours) in an aqueous liquor at 30-35° C., the liquor ratio being 1:20, which contains 20 per cent of ethylene imine

calculated on the weight of the silk. After rinsing and souring with a solution of acetic acid containing 2 grams per liter for half-an-hour at 60° C. the silk yields a good black when dyed with 8 per cent of Azo Acid Black 3 BL in presence of 4 per cent of acetic acid at 40 to 80° C. A silk which has not been aminated is only tinted light blue in the same bath.

If before the action of the imine the same acetate silk is treated in presence of the equivalent quantity of sodium acetate with a reaction product from N-butylamine chlorohydrate and 3.2 moles epichlorhydrin, the affinity is further increased.

9. A solution of 20 per cent strength in glycol-methylene-ether (glycol formal) of 90 parts of acetyl cellulose having 58.2 per cent of bound acetic acid and containing 10 parts of mixed polymerizate from 1 mol maleic acid anhydride and 1 mol vinylmethyl ether is cast to films. These are suspended over-night above ethylene imine (20 per cent), the temperature being 60° C. They then exhibit a strong affinity for acid dyestuffs such as Fast Red AV (Schultz Farbstofftabellen, 7th ed., vol. I, page 92) or Alizarine Direct Violet ER (Schultz Farbstofftabellen, 7th ed., vol. II, page 10).

10. An artificial silk from cellulose nitrate spun from the solution in acetone and dioxane and containing 10 per cent of the mixed polymerizate of vinyl ethyl ether and maleic acid anhydride in the molecular ratio 1:1 is denitrated by means of a solution of 12 per cent strength of ammonium hydrosulfide; it is then washed first with a solution of 5 per cent strength of common salt, then with common salt solution containing 2 per cent of hydrochloric acid or sulfuric acid and thoroughly rinsed. By after-treatment with an aqueous ethylene imine solution of 10 per cent strength at 40° C. and a short heating to 80° C. the silk becomes a strongly basic fibrous material which can easily be dyed with acid wool dyestuffs. The fastness of the dyeings, for instance that with 4 per cent of Alizarinecyanine Green G Extra is improved if the aminated fiber is treated before or after dyeing or simultaneously with the fixing of the dyestuff with an alkylating agent, for instance epichlorhydrin. Thus the silk impregnated with the dyestuff solution may be dried and the dyeing fixed by heating for 4 hours at 70° C. and 75 per cent relative moisture in presence of vapor of chlorhydrin.

11. Acetate artificial silk which contains 15 per cent of the esterification product of acetyl cellulose having 50 per cent of bound acetic acid and maleic acid anhydride or succinic acid anhydride is partially and permutoid saponified by exposure at a temperature of 70° C. for about 8 hours at a 75 per cent relative moisture by means of 8 per cent of ammonia in the gaseous phase. It is then after-treated with 10 per cent of ethylene imine in the form of vapor for 8 hours at 60° C. The silk is then capable of being dyed with acid and substantive dyestuffs.

12. Viscose artificial silk is mordanted with tannin and tartrametic in the usual manner and then treated with 10 per cent of hexa- $[\gamma\text{-chloro-}\beta\text{-hydroxypropyl}]\text{diethylene}$ ammonium chloride in presence of an equivalent quantity of sodium acetate in a liquor ratio of 1:20 and at 20-70° C. The fiber thus prepared easily reacts with a solution of about 10 per cent strength of ethylamine. The latter, however, may be used in the form of vapor. The treated silk is dyed very well by acid dyestuffs. Dyeings with substantive dye-

stuffs are improved considerably in their fastness, particularly if the basic character of the after-treatment with the alkylating agent is reinforced by means of an isothio urea ether or cyanamide.

Also viscose artificial silk which has been mordanted with tannin and tartrametic alone and then treated with vapor of ethylene imine (15-20 per cent) at 70° C. exhibits an affinity to acid dyestuffs such as Orange II. The dyeing is comparatively fast to washing, but not so good as when an intermediate treatment with tetra- $[\gamma\text{-chloro-}\beta\text{-hydroxypropyl}]\text{ ammonium chloride}$ follows the mordanting.

13. Cellulose film which contains 8 per cent of the polymeric carboxylic acid produced by splitting the mixed polymerizate from vinyl ethyl ether and maleic acid anhydride is suspended for 2 hours at 80° C. in vapor of ethylene imine. The material cut into narrow bands may serve as an effect material for the hat industry and may be dyed fast to light and water with acid dyestuffs, for instance those of the anthraquinone series, such as Alizarine Direct Blue A.

14. A band of viscose fiber is treated first with the sulfurized phenol sold in commerce under the trade mark "Katanol ON" and then with a bath which contains tetra- $[\gamma\text{-chloro-}\beta\text{-hydroxypropyl}]\text{ ammonium chloride}$ and sodium acetate of which only about 8 to 10 per cent is taken up by the fiber. The rinsed material is cut to staple and then after-treated with an aqueous ethylene imine solution of 8 per cent strength at 40° C.

15. A film of cellulose ethyl ether containing 42 per cent of ethoxyl and 10 per cent of the mixed polymerizate from vinyl chloride and maleic acid anhydride is first treated for several hours with water at 60-70° C. and then aminated by means of 15 per cent of C-methylethylene imine in the gas phase. The film is dyed by means of Orange II.

16. A film of cellulose ethyl ether containing 42 per cent of ethoxyl and 12 per cent of the mixed polymerizate from vinyl ethyl ether and maleic acid anhydride is treated for 8 hours with 15 per cent of ethylene imine at 75 per cent of relative moisture. It now shows essentially increased affinity for acid dyestuffs, such as Alizarine Direct Blue A or Metanil Yellow (Schultz Farbstofftabellen, 7th ed., vol. I, page 78).

17. A film of polyvinyl formal which contains 10 per cent of a "Novolak" from 1 mol phenol and 6.5 mol formaldehyde is treated under conditions given in Example 14 with ethylene imine. The film is now dyed strongly by Orange II.

18. A natural silk is mordanted with tannin and tartrametic and then treated in a solution of 30-60° C. containing 10 per cent of hexa- $[\gamma\text{-chloro-}\beta\text{-hydroxyethylene}]\text{ diammonium chloride}$ and the equivalent quantity of sodium acetate. It is then treated at 30-40° C. with an aqueous ethylene imine solution of 7 per cent strength. The silk is thus given a considerably increased affinity for acid dyestuffs. Fabrics which have been made of silk treated in the manner described in this example and nitrated silk yield when dyed with acid or basic dyestuffs or with both types of dyestuff powerful effects. Fibroin artificial silk behaves in analogous manner.

19. An acetate artificial silk containing 10 per cent of the polymeric acid from a mixed polymerizate of 1 mol vinyl chloride and 1 mol maleic acid anhydride is soaked with 15 per cent of the

product of reaction of ethylene diamine with 4 mol 1:2-propylene sulfide in presence of 3 per cent of sodium hydrosulfite at 50 to 70° C. After a short treatment the silk is after-treated with an ethyleneimine solution of 8 per cent strength at 40° C. After a short time a strong effect is produced. After acidifying the silk may be dyed with 4 per cent of Alizarinecyanine Green G Extra in presence of 4 per cent of acetic acid. The dye bath is rapidly exhausted at medium temperatures (50-75° C.)

20. A film of cellulose ethyl ether containing 42-43 per cent of ethoxyl and 10 per cent of the chlorinated resin from xylene and formaldehyde which has been caused to react with potassium hydrosulfide in alcohol and subsequently acetylated is heated in presence of alcohol vapor as a swelling agent with 10 per cent of ethyleneimine and 3 per cent of trimethylamine for 8 hours at 60° C. The film may now be dyed with suitable acid dyestuffs, for instance Metanil Yellow.

21. Copper silk which has been swollen by means of caustic soda lye of 4 per cent strength and then thoroughly wetted is impregnated with a solution of 10 per cent strength of ammonium glycerine-tris-phthalate at room temperature, then centrifuged, dried and acidified with dilute hydrochloric acid for fixing the acid on the fiber. A silk thus prepared is suspended for 4 hours at 60° C. in ethyleneimine vapor. It may now be dyed after preliminary acidifying in intense tints by means of acid dyestuffs. Instead of acidifying to fix the acid this object may be attained by heating. In similar manner other polycarboxylic acids and compounds equivalent in the sense of the invention, for instance aromatic tricarboxylic acids, pyridine-polycarboxylic acids, aromatic polycarboxylic acids, such as di-hydroxynaphthalene-dicarboxylic acids, may be used.

22. Cuprammonium artificial silk which has been swollen by means of 0.5 normal sodium hydroxide and which has subsequently been washed free of alkali, is impregnated at room temperature with an aqueous solution containing 10 per cent of the sodium salt of pentaerythrit-tetraphthalic acid, centrifuged and aftertreated after slight drying with a solution containing 1 per cent of the reaction product of dodecyl-triethylene-tetraminehydrochloride and 9 mols epichlorhydrin. Silk pretreated in this manner is now treated for 4 hours at 60° C. and 75 per cent relative moisture with 15 per cent of ethyleneimine. The artificial silk animalized in this manner shows a marked affinity for acid dyestuffs for wool.

23. Acetate artificial silk produced according to the process disclosed in my copending application Ser. No. 47,638, filed October 31, 1935, which contains 10 per cent of a mixed polymerizate from 1 mol vinylmethylether and 1 mol maleic acid anhydride is heated in a closed vessel at 75 per cent relative moisture for 12 hours at 90° C. together with 15 per cent cyclohexylethyleneimine absorbed in diatomaceous earth, the content of the vessel being 60 parts of volume for 1 part of the fiber by weight. After thorough acidifying with a solution of 0.5 per cent of formic acid at 60° C. the fiber which contains about 1.2 per cent of nitrogen is dyed with 8 per cent Diamond Black PBB (Schultz Farbstofftabellen, 7th ed., vol. I, page 104) at 40 to 85° C. in the presence of 3 per cent of acetic acid. By afterchroming for half-an-hour with a solution of 2.5 per cent of potassium bichromate and 2 per cent

of formic acid at 90 to 95° C. a coloring which is fast to washing and fulling is obtained.

In case light tints are desired the silk which has slightly yellowed in the course of the amination may be bleached without any loss of affinity for the acid dyes.

24. Acetate artificial silk containing 10 per cent of acetyl cellulose maleic ester-acid (produced from partly acetylated acetyl cellulose and maleic acid anhydride) is treated at 70° C. and 75 per cent relative moisture for 7 hours with 12 per cent of ethyleneimine in vapor form. The silk contains about 1.5 to 2 per cent nitrogen. It is intensely dyed with acid dyestuffs.

25. Acetate artificial fiber containing 8 per cent of a soluble condensation product from 10 mol phenol and 8 mol formaldehyde obtained in an acid medium, is treated in the same manner as indicated in the previous examples with ethyleneimine. The fiber is intensely dyed with many acid dyestuffs such as for instance Alizarine Direct Blue A.

26. Acetate artificial fiber containing 8 per cent of a mixed polymerizate from 1 mol vinylmethylether and 1 mol maleic acid anhydride or 1 mol vinylacetate and 1 mol maleic acid anhydride and 4 per cent of the soluble condensation product from 10 mol phenol and 8 mol formaldehyde is aminated in the manner indicated in the previous examples at 70° C. with the aid of 5 per cent ethyleneimine. A fiber is obtained which contains up to 3 per cent nitrogen and which is intensely dyed by a great many acid dyestuffs.

27. A film prepared from hydroxyethyl cellulose soluble in alkali, which contains about 8 per cent cellulose glycolic acid is treated for 4 hours at 60° C. with 12 per cent ethyleneimine. The film now shows strong affinity for acid dyestuffs, for instance Alizarinecyanine Green G Extra. The affinity is enhanced if the film is treated before amination with a solution containing 1 per cent of tetrachlorohydroxypropyl ammonium chloride.

In the claims following hereafter the expression "having incorporated and fixed therein" indicates that the compounds in question must not be removable or at most with difficulty removable from the substratum by washing with water.

The treatment of materials in which the acid hydroxyl group is bound to protein residues is not within the scope of the appended claims.

What I claim is:

1. A process of increasing the affinity of fibrous materials and films for acid and substantive dyestuffs said materials having incorporated throughout and fixed within the body thereof an acid reacting resinous component having in its molecule a member of the group consisting of the carboxyl group, the phenolic hydroxy group, and the mercapto-alkyl group, which comprises reacting on said materials an amine containing in its molecule a halogenalkyl group and treating said materials with an alkyleneimine.

2. A process of increasing the affinity of fibrous materials and films for acid and substantive dyestuffs said materials having incorporated throughout and fixed within the body thereof an acid reacting resinous compound having in its molecule a member of the group consisting of the carboxyl group, the phenolic hydroxy group, and the mercapto-alkyl group, which comprises reacting on said materials an amine containing in its molecule halogeno- β -hydroxy-propyl groups and treating said materials with an alkyleneimine.

3. A process of increasing the affinity of fibrous materials and films for acid and substantive dye-stuffs said materials having incorporated throughout and fixed within the body thereof an acid reacting resinous component having in its molecule a member of the group consisting of the carboxyl group, the phenolic hydroxy group, and the mercaptoalkyl group, which comprises reacting on said materials an amine containing in its molecule γ -chloro- β -hydroxypropyl groups and treating said materials with an alkylene imine.

4. A process of increasing the affinity of fibrous materials and films for acid and substantive dye-stuffs, said materials having incorporated throughout and fixed within the body thereof an acid reacting resinous component containing in its molecule besides one of the group consisting of

the carboxyl group, the phenolic hydroxy group and the mercapto-alkyl group halogen alkyl groups, which comprises reacting on said materials an amine and treating said materials with an alkyleneimine.

5. A process of increasing the affinity of fibrous materials and films for acid and substantive dye-stuffs, said materials having incorporated throughout and fixed within the body thereof an acid reacting resinous component containing in its molecule besides one of the group consisting of the carboxyl group, the phenolic hydroxy group and the mercapto-alkyl group alkylating groups, which comprises reacting on said materials an amine, and treating said materials with an alkylene imine.

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