

1

3,551,087

## SIMULTANEOUS DYEING AND BLEACHING OF PROTEINACEOUS FIBROUS MATERIAL

Oswald Schmidt, Frankenthal, Pfalz, Germany, assignor to Badische Anilin- & Soda-Fabrik Aktiengesellschaft, Ludwigshafen (Rhine), Germany

No Drawing. Filed Sept. 29, 1965, Ser. No. 491,441  
Claims priority, application Germany, Oct. 2, 1964,

1,469,607, 1,469,608

Int. Cl. D06p 5/00, 7/00

U.S. Cl. 8-19

9 Claims

### ABSTRACT OF THE DISCLOSURE

Process for simultaneously dyeing and bleaching a proteinaceous fibrous material in which the fibers are treated at an elevated temperature as required for dyeing wool in a neutral or acid aqueous liquor containing (a) an acid dye stable to peroxides, (b) performic acid which is preferably being formed in said liquor during the treatment, and (c) an oxygen stabilizer.

Proteinaceous fibrous material, such as animal hair, particularly wool and silk, fiber mixtures containing the same and materials prepared therefrom, are as a rule dyed at elevated temperature, i.e. at 80° to 100° C. or under superatmospheric pressure at above 100° C. in non-alkaline liquors; the liquors generally contain conventional so-called wool dyes and may optionally contain dyeing assistants, for example leveling agents.

It is often necessary or desirable to bleach the proteinaceous fibrous material so that the dyes may have full action. It has hitherto been customary to carry out the said bleaching in alkaline liquors which contain about 3 to 10 g./l. of 100% hydrogen peroxide, equivalent to about 1.5 to 5 g./l. of active oxygen, and a peroxide stabilizer, for example an alkali metal pyrophosphate or a complex-forming polyphosphate.

Since a neutral to acid medium is required for the dyeing of wool with so-called wool dyes, the two operations of bleaching and dyeing cannot be carried out at the same time in the same liquor. Simultaneous bleaching and dyeing, however, would be very desirable because the treatment of the wool could be greatly simplified in this manner.

It is, therefore, an object of this invention to provide a method of bleaching and dyeing proteinaceous fibrous material in a particularly simple way in one operation. It is a further object of the invention to provide a process in which the active oxygen which causes the bleaching becomes available gradually during the reaction period. Further objects will be apparent from the description.

These objects, namely a process for the simultaneous dyeing and bleaching of proteinaceous fibrous material, particularly silk and wool, are achieved by treating the proteinaceous fibers with a non-alkaline aqueous dye liquor which contains (a) a so-called "acid wool dye" which is an acid dyestuff capable of dyeing wool and which must also be stable to peroxides, and (b) performic acid formed, preferably in situ, by reaction of hydrogen peroxide with a substance capable of splitting off formaldehyde under the reaction conditions, a low molecular

2

weight formic acid alkanol ester and/or a low molecular weight formaldehyde, 0.2 to 10 grams/liter, preferably 0.5 to 2 grams/liter, of active oxygen being made available in the dye liquor during the treatment of the fibers. A conventional peroxide stabilizer, also referred to as an oxygen stabilizer, is also used in the non-alkaline aqueous liquor.

We mean by active oxygen, oxygen which is set free from hydrogen peroxide when it is converted quantitatively to water.

Substances yielding formaldehyde are defined as substances which contain at least once a group having the general formula:



in which Y denotes a nitrogen or oxygen atom, X denotes a nitrogen or oxygen atom or the group  $-SO_3M$  in which M is a proton, an ammonium ion, an alkali metal ion or half an alkaline earth metal ion, and the valencies of the said nitrogen and/or oxygen atoms which are not attached to the central carbon atom being, in the absence of a  $SO_3M$  group, at the most partly saturated by hydrogen.

Examples of substances which contain at least once a group having the Formula I are: formaldehyde polymers, such as trioxymethylene, tetraoxymethylene and paraformaldehyde; low molecular weight formals, such as dimethylformal and diethylformal hydroxymethanesulfonic acid; aminomethanesulfonic acid; imino-bis-methanesulfonic acid and low molecular weight N-alkyl and N-hydroxyalkyl derivatives of these two acids; nitrolo-trimethanesulfonic acid, alkali metal salts and alkaline earth metal salts of these acids, such as preferably the sodium, potassium and calcium salts; N-methylol compounds of carbamides, such as particularly urea, imidazolines, tetrahydrotriazinones, hexahydropyrimidones and urones; of melamines, of dicyanodiamide; and also ethers of such N-methylol compounds with alcohols having one to five carbon atoms.

Examples of low molecular weight formic alkanol esters and formamides are substances having the general formula



in which Q denotes a radical  $-OR$  or



R being an alkyl radical having one to five carbon atoms,  $R^1$  being a hydrogen atom or an alkyl radical having one to five carbon atoms and  $R^2$  being a hydrogen atom or an alkyl radical having one to five carbon atoms. Examples of substances having the Formula II are: methyl formate, ethyl formate, propyl formate, butyl formate and diethylformamide.

The term "low molecular weight" in the present application means compounds which contain no alkyl groups or contain alkyl groups having one to five carbon atoms.

Particularly advantageous results are obtained when the substances which split off formaldehyde or low molecular weight formamides used or additionally used are those

3

which form ammonia or amines by reaction with hydrogen peroxide. This feature results in the drop in the pH of the dye-bleach liquor otherwise occurring during simultaneous dyeing and bleaching owing to the formation of formic acid being either prevented or minimized. In this manner optimum dyeing and bleaching conditions in terms of a specific pH range are always maintained. A particularly suitable and therefore preferred substance of this type is hexamethylenetetramine. Formamide, dimethylformamide, aminomethanesulfonic acid, imino-bis-methanesulfonic acid, and derivatives bearing alkyl radicals at the nitrogen atoms, particularly the methyl derivatives and the salts, however, act in the same way.

Substances of the abovementioned type are reacted with hydrogen peroxide in aqueous medium. The speed of this reaction is dependent on the hydrogen ion concentration of the medium. An acid or neutral range is used to achieve rapidly a bleaching solution which is ready for use. The acid reaction may be produced by adding inorganic or organic acids or acid salts. The acids may be chosen at will. Strong acids are very suitable, such as sulfuric acid and sulfonic acids, and acid salts such as sodium bisulfite and sodium bisulfate. The amount of acid substance required depends on its acidity. Amounts of 0.5 to 10% of strong acids, with reference to the weight of hydrogen peroxide to be reacted, are adequate, whereas 10 to 50% of weaker acids or acid salts may be necessary. It seems as though even in acid solution, the reaction to form performic acid does not immediately proceed to the point of completely exhausting one reaction component; possibly an equilibrium condition is set up which continues during bleaching and consequently during consumption of performic acid, as long as all the reactants are still present.

The ratio between (a) formaldehyde as obtained from compounds which are capable of splitting off formaldehyde, low molecular weight formic acid alkanol esters or low molecular weight formamides, and (b) hydrogen peroxide is preferably chosen so that for each mole of said esters and amides or each mole of formaldehyde available from the compounds splitting off formaldehyde, 1 to 12 moles of hydrogen peroxide is available; particularly successful results are achieved with a molar ratio of (a):(b) falling within a range of about 1:3 to 1:10.

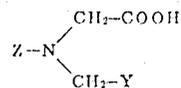
The amount of hydrogen peroxide depends on whether it is desired to bleach in a long liquor or with a padding liquor. Amounts of 35% hydrogen peroxide of from 10 to 30 ccm./l have proved to be particularly useful for long liquors and from 40 to 130 ccm./l for padding liquors.

The performic acid may be prepared by adding the ingredients, in the amounts desired for bleaching, direct to the liquor which already contains dye and dyeing assistants. Alternatively a concentrated stock bleaching solution may first be prepared which is diluted to the final concentration shortly prior to use or added in the necessary amount to the liquor containing dye and dyeing assistants. Stock bleaching solutions may be prepared in concentrations which are equivalent to 100 to 500 ccm./l of 35% hydrogen peroxide. When preparing stock bleaching solutions it is recommended that the temperature should not exceed 40° C; bleaching liquors to which the ingredients are added direct may however be prepared at higher temperatures, i.e. temperatures up to about 60° C.

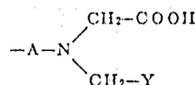
For simultaneous dyeing and bleaching according to the present invention, liquors are required which contain conventional oxygen stabilizers. It is advantageous to add these stabilizers during the formation of the performic acid. The following may be given as examples of stabilizers which may be used alone or mixed together: magnesium silicate, magnesium phosphate, polysulfonic acids or acid salts, for example citric acid, tartaric

4

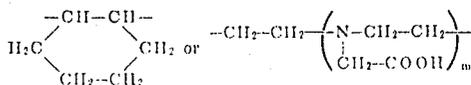
erably polymerized chain phosphates having the general formula:  $M_{n+2}P_nO_{3n+1}$ , in which M denotes the radical of an alkali metal, particularly of sodium or potassium, and  $n$  denotes one of the integers from 2 to 10, such as tetra-alkali pyrophosphates, alkali tripolyphosphates and more highly condensed phosphates, such as alkali metal tetrapolyphosphates, to heptapolyphosphates, and particularly complex-forming aminopolycarboxylic acids, especially those having the general formula:



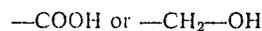
in which Z denotes the radical  $\text{-CH}_2\text{-COOH}$  or



A denotes a radical having the formula:



$m$  denotes one of the integers zero, 1 or 2 and Y denotes a radical having the formula



such as N-hydroxyethylethylenediaminetetraacetic acid, o-cyclohexylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, triethylenetetraminehexaacetic acid, N-hydroxyethyldiethylenetriaminetetraacetic acid and particularly nitrilotriacetic acid and ethylenediaminetetraacetic acid and the ammonium, magnesium, alkali metal and alkaline earth metals salts, particularly the magnesium-sodium, magnesium-potassium, sodium and potassium salts of these acids. The said phosphates have only a relatively slight stabilizing effect in the said method and they are therefore used in large amounts, i.e. twice to thirty times, preferably three to fifteen times the weight of active oxygen available. Complex-forming aminopolycarboxylic acids or their salts of the abovementioned types are therefore preferred as stabilizers; 0.1 to once, preferably 0.25 to 0.5 the weight of active oxygen available is enough of these stabilizers. Particularly good results are often achieved with mixtures of complex-forming aminopolycarboxylic acids or their salts and the said phosphates. These mixtures may be used in the same small amounts as the complex-forming aminopolycarboxylic acids and often give a better bleaching effect than the said substances alone.

The production of performic acid is particularly convenient and advantageous when, a stable composition is prepared which contains in the correct proportions the components which in water with hydrogen peroxide will give a bleaching liquor ready for use. A particularly advantageous stock composition of this type contains 50 to 20% by weight of hexamethylene tetramine, 30 to 60% by weight of hydroxymethanesulfonic acid or its ammonium, alkali metal (particularly sodium or potassium), or alkaline earth (particularly calcium) salts, 10 to 17% by weight of polymeric linear alkali metal phosphates, particularly sodium or potassium phosphates, and 10 to 3% by weight of ethylenediaminetetraacetic acid or its ammonium, alkali metal (particularly sodium or potassium), or alkaline earth metal (particularly magnesium) salts. Moreover the composition may contain acid, sodium hydrogen sulfate and potassium hydrogen phosphate. Such a composition may be used for example as follows: for each liter of bleaching liquor, 20 ccm.

of 35% hydrogen peroxide is mixed with 20 ccm. of water, 3 to 7 g. of the composition is dissolved therein and the solution is made up to 1 liter with water.

Performic acid obtainable in accordance with the directions given above may be added to the dye liquor in the form of solutions of any concentration, if it is not prepared from the start in the dye liquor. Since performic acid decomposes readily, it is recommended not to prepare it until shortly before it is to be used.

The new method may be applied very simply. As in prior art dyeing methods, the working conditions are adapted particularly to the dyes being used. In particular the pH value of the liquor, which is usually from 1 to 7, is chosen to provide those conditions especially favourable for the particular dye or dyes. In contrast to conventional dyeing methods, there is only one restriction, namely that wool dyes which are resistant to peroxides must be used. Dye manufacturers give details of the behavior of their dyes with respect to peroxides in their pattern cards or other technical literature. In other respects, the dyes used may belong to the conventional classes for wool dyeing. In general, "acid wool dyes" are used for the process of the invention, for instance the dyes listed as "acid dyes" in the Colour Index 1956, 2nd edition, and marked as being suitable for dyeing wool. Acid azo dyes, acid anthraquinone dyes, 1:1 metal complex dyes and 1:2 metal complex dyes may be given as examples of the most important classes. In addition to performic acid, the dye or dyes and agents for regulating the pH value, the liquors may contain the conventional assistants for dyeing proteinaceous fibrous material, for example leveling agents, wetting agents, carriers, dispersing agents, buffer salts, neutral salts and fiber protectives.

Working with bleaching dye liquors prepared in accordance with the above statements is analogous to conventional dyeing of proteinaceous fibrous material. Thus for example the material to be treated may be added to the liquor heated to about 50° C., the liquor heated to boiling point and kept at boiling temperature for about one hour. It is also possible to use the high-temperature method, i.e. to carry out the treatment under pressure at temperatures above 100° C. with a corresponding shortening of the treatment time. Another possibility, particularly suitable for tops and piece goods, is continuous dyeing and bleaching by padding and steaming. The dyed and bleached material is rinsed hot and cold in the usual way. Further processing of the treated material is as usual.

If the combined dyeing and bleaching liquor is to be used only once it is advantageous economically to choose a content of bleaching agent which is not too high. Amounts of bleaching agent corresponding to 0.5 to 2 g./l. of active oxygen have been found to be adequate. There is however also the possibility of using one and the same liquor several times, the amounts of dye and chemical reagents which have been used up being replenished. In this so-called standing bath method, it is possible to use the same liquor six to eight times.

The present process may also be combined with other wet finishing methods, in the treatment of wool and wool mixtures, for example, with a brightening or an antifelt finishing by chlorination. It is easily possible to carry out all these treatments in the same liquor. Brightening in the same liquor is preferably carried out during the bleaching and dyeing or after the same. For the antifelt finish, the liquor may first be charged for example with elementary chlorine or substances yielding chlorine, such as dichlorocyanuric acid or its salts, particularly alkali metal salts, such as sodium and potassium salts, substances for regulating the pH value, anti-swelling agents and the like and, following the treatment of the fibrous material with chlorine, which usually takes place at room or slightly elevated temperature, the abovementioned substances for bleaching and dyeing are added to the same liquor. Then at the same time, without the additional measures otherwise conventionally used, an oxidizing antichlorination

takes place, i.e. the unused chlorine is rendered innocuous. A further simplification is possible by carrying out the chlorine treatment and the bleaching and dyeing at the same pH value. The pH value may be adjusted for all steps of the process prior to the commencement of the chlorine treatment.

The advantages of the new process lie in a considerable shortening and simplification of the course of the treatment.

The invention is illustrated by the following examples.

#### EXAMPLE 1

100 kg. of washed loose wool is pressed in the usual way into the material carrier of an alloyed steel pack dyeing machine which holds about 1,000 liters of liquor. The machine is first filled with about 900 liters of water and circulation is commenced in order to expel the bulk of the air from the woolen material. Then 10 liters of 35% hydrogen peroxide is added and then 3 kg. of a mixture of:

	Parts
Sodium hydroxymethanesulfonate -----	56
Hexamethylene tetramine -----	23
Sodium tripolyphosphate -----	15
Ethylenediaminetetracetic acid -----	6

is dissolved in the liquor. The liquor is heated to 50° C., 10 kg. of anhydrous sodium sulfate and 8 kg. of ammonium acetate are added and the whole is made up to about 1,000 liters. 50 g. of the dye C.I. Acid Blue 59 (C.I. 50,315) is dissolved in a little water and added to the liquor. The liquor is heated to boiling temperature in about thirty minutes and left at boiling temperature for forty to forty-five minutes. Then 1.5 liters of 60% acetic acid is added and the whole again left at boiling temperature for twenty-five to thirty minutes. The goods are then rinsed with water in the usual way. A pale blue dyeing is obtained which is just as beautiful and bright as when the goods have been bleached prior to dyeing.

After dyeing is over, the liquor may be removed and after appropriate replenishment with active oxygen, i.e. with hydrogen peroxide and the abovementioned mixture, dye and other additives, may be used for one or more further dyeing batches.

#### EXAMPLE 2

An alloyed steel dyeing machine for tops bobbins is used which holds 1,500 liters of liquor. About 1,250 liters of water is first introduced into the machine and then the bobbins with 100 kg. of unbleached wool tops are introduced. With the circulation pump running, the water is heated to about 50° C. and then 1 liter of 60% acetic acid is added and also 15 liters of 35% hydrogen peroxide, 2.2 kg. of sodium iminobismethanesulfonate, 1.1 kg. of hexamethylene tetramine, 0.5 kg. of ethylenediaminetetracetic acid and 0.5 kg. of sodium pyrophosphate. The pH value is adjusted to about 4.5 with acetic acid. 250 g. of the sodium salt of the acid sulfuric acid ester of an adduct of 1 mole of sperm oil alcohol and 80 moles of ethylene oxide and 400 g. of an adduct of 1 mole of oleylamine and 10 moles of ethylene oxide are added as a leveling agent and then 100 g. of the dye C.I. Acid Blue 62 (C.I. 62,045) which has previously been dissolved in water. The liquor is then made up to 1,500 liters with water. It is heated to boiling point in about fifteen minutes and left at the boiling temperature for one hour. The goods are rinsed with water in the usual way. A pale blue dyeing is obtained which is just as beautiful and bright as on previously bleached goods.

#### EXAMPLE 3

About 2,250 liters of water is placed in an alloyed steel cheese dyeing machine which holds about 2,500 liters, the material carrier with 250 kg. of precleaned woolen yarn in the form of cheeses is introduced into the apparatus and the circulation pump is switched on, in order to expel

7

the bulk of the air from the cheeses. 20 liters of 35% hydrogen peroxide and 6 kg. of a mixture of

	Parts
Sodium nitrilomethanesulfonate .....	50
Hexamethylene tetramine .....	20
Ethylenediaminetetracetic acid .....	10
Sodium tripolyphosphate .....	20

are dissolved in the liquor. The liquor is then heated to about 50° C., 25 kg. of anhydrous sodium sulfate and 20 kg. of ammonium acetate are added and the whole is made up to 2,500 liters with water. 375 g. of the dye C.I. Acid Blue 90 (C.I. 42,655) is dissolved in water and added to the liquor, which is then heated to boiling temperature within twenty to thirty minutes and kept at this temperature for forty to forty-five minutes. 3.7 liters of 60% acetic acid is added and dyeing is continued for another twenty to thirty minutes at the boiling temperature. The material is then rinsed in the usual way. A bright pale blue dyeing is obtained which is just as beautiful and bright as on previously bleached material.

The exhausted liquor may be appropriately replenished with active oxygen, i.e., with hydrogen peroxide and the abovementioned mixture, dye and other additives and used again for one or more further batches for dyeing.

#### EXAMPLE 4

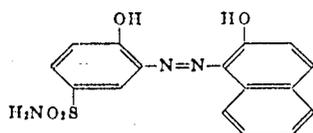
The procedure of Example 3 is followed with the exception that with the 25 kg. of anhydrous sodium sulfate there is added to the initial water 12 kg. of concentrated sulfuric acid instead of the 20 kg. of ammonium acetate. 250 g. of C.I. Acid Blue 45 (C.I. 63,010) is used instead of C.I. Acid Blue 90.

#### EXAMPLE 5

About 1,800 liters of water is placed in an alloyed steel suspension machine which will hold 2,000 liters of liquor, and 10 liters of 35% hydrogen peroxide and 3 kg. of a mixture of:

	Parts
Trioxymethylene .....	57
Sodium iminomethanesulfonate .....	20
Sodium pyrophosphate .....	15
Ethylenediaminetetracetic acid .....	8

are dissolved therein. 1.5 kg. of 60% acetic acid and 0.5 kg. of the sodium salt of the acid sulfuric ester of an adduct of 1 mole of sperm oil alcohol and 80 moles of ethylene oxide are added and the whole is made up to 2,000 liters with water. 200 g. of the dye:



in the form of its 1:2 chromium complex is dissolved in water and added to the liquor and while the latter is being circulated continuously, the material carrier, on which 100 kg. of unbleached precleaned woollen yarn is suspended, is introduced into the liquor. The liquor is brought to boiling temperature within forty to forty-five minutes and then dyeing carried out for forty to forty-five minutes at the boiling temperature. The material is then rinsed with water in the usual way. A beautiful pale violet dyeing is obtained which is just as bright as on previously bleached yarn.

#### EXAMPLE 6

100 kg. of precleaned woollen yarn is chlorinated in the following way in an alloyed steel suspension machine having a capacity of 1,500 liters:

The yarn is prewetted with 0.2 kg. of nonylphenol octaglycol ether for about ten minutes in about 1,500 liters of cold water at 10° to 20° C. The material carrier is then withdrawn, 10 kg. of anhydrous sodium sulfate is

8

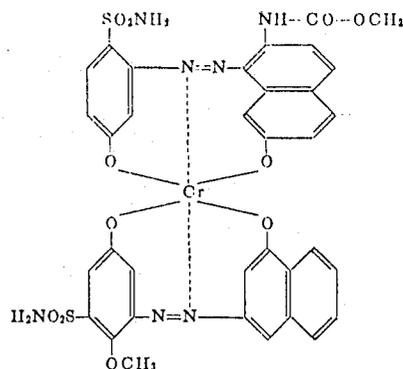
dissolved in the wetting liquor, then a previously prepared solution of 2.5 kg. of anhydrous tetrasodium pyrophosphate and 4 kg. of potassium dichloroisocyanurate in about 50 to 60 liters of water is added to the liquor which is adjusted with acetic acid to a pH value of about 5. The material carrier is then reintroduced and the yarn is chlorinated for thirty to sixty minutes at 10° to 20° C. with the circulation pump running. If the active chlorine present is not being absorbed quickly enough by the wool, the temperature may be raised to 25° to 30° C. for ten to fifteen minutes before the end of the chlorination.

8 kg. of ammonium acetate, 15 liters of 35% hydrogen peroxide and 4.5 kg. of the mixture according to Example 1 are then added to the same liquor. Heating up of the liquor is then commenced and an aqueous solution of 50 g. of C.I. Acid Blue 59 (C.I. 50,315) is added at once. Boiling temperature is reached in thirty minutes and this temperature is maintained for forty to forty-five minutes. Then 1.5 liters of 60% acetic acid is added and dyeing is completed in another twenty to thirty minutes. The dyed yarn is rinsed with water in the usual way and the material carrier is withdrawn from the machine.

A non-felted, creaseproof yarn having a pale blue color, whose brightness is equivalent to that of a dyeing on a separately bleached yarn, is obtained in one and the same liquor.

#### EXAMPLE 7

About 900 liters of water is placed in an alloyed steel winch dyeing machine having a liquor capacity of 1,000 liters, and 0.75 liter of 60% acetic acid, 1 kg. of ammonium sulfate and 125 g. of the sodium salt of the acid sulfuric ester of an adduct of 1 mole of sperm oil alcohol and 80 moles of ethylene oxide are dissolved therein. 5 liters of 35% hydrogen peroxide, 0.8 kg. of dimethylolurea, 80 g. of hexamethylene tetramine, 120 g. of sodium bisulfite, 270 g. of sodium bisulfate, 150 g. of sodium pyrophosphate and 135 g. of ethylene diaminetetracetic acid are dissolved in the liquor. Finally 50 g. of the dye having the formula:



is dissolved in water and added to the liquor and the liquor is made up to a total of 1,000 liters with water. 50 kg. of unbleached precleaned woollen piece goods is then introduced into the liquor, ten minutes is allowed to elapse for wetting of the material, and the liquor is then heated to boiling temperature within forty to forty-five minutes and kept at boiling temperature for another forty to forty-five minutes. The liquid is then drained off and the material is rinsed in the usual way. A beautiful pale grey dyeing is obtained.

#### EXAMPLE 8

100 kg. of washed loose wool is pressed in the usual way into the material carrier of an alloyed steel pack dyeing machine having a capacity of about 1,000 liters of liquor. The machine is first filled with about 900 liters of water and the circulation is switched on in order to

9

expel the bulk of the air from the wool. 10 liters of 35% hydrogen peroxide, 0.45 kg. of sodium tripolyphosphate and 0.18 kg. of ethylenediaminetetracetic acid are added and 1.5 liters of 10% sulfuric acid and 1 liter of formamide are dissolved in the liquor. The liquor is then heated to 50° C., 10 kg. of anhydrous sodium sulfate and 8 kg. of ammonium acetate are added and the whole is made up to about 1,000 liters with water. 50 g. of the dye C.I. Acid Blue 59 (C.I. 50,315) is dissolved in a little water and added to the liquor. The liquor is heated to boiling temperature within about thirty minutes and left at boiling temperature for forty to forty-five minutes. 1.5 liters of 60% acetic acid is then added and the whole left at boiling temperature for another twenty-five to thirty minutes. The material is then rinsed in the usual way. A pale blue dyeing is obtained which is just as beautiful and bright as when the material has been bleached prior to dyeing.

When dyeing is over, the liquor may be removed and used again for one or more further dyeing batches after it has been appropriately replenished with active oxygen, i.e., with hydrogen peroxide and formamide, dye and conventional additives.

## EXAMPLE 9

An alloyed steel dyeing machine for tops bobbins is used which has a capacity of 1,500 liters of liquor. About 1,250 liters of water is first placed in the machine and the bobbins are introduced with 100 kg. of unbleached wool tops. With the circulation pump running, the liquor is preheated to about 50° C. and then 1 liter of 60% acetic acid, 0.5 kg. of ethylenediaminetetracetic acid and 0.5 kg. of sodium polyphosphate are added together with 22.5 liters of a stock bleaching solution prepared previously from

15 liters of 35% hydrogen peroxide  
2.3 liters of 10% sulfuric acid and  
5.2 liters of dimethylformamide.

The pH value is adjusted to about 4.5 with acetic acid. 250 g. of the sodium salt of the acid sulfuric acid ester of an adduct of 1 mole of sperm oil alcohol and 80 moles of ethylene oxide and 400 g. of an adduct of 1 mole of oleylamine and 10 moles of ethylene oxide are added as a leveling agent and then 100 g. of the dye C.I. Acid Blue 62 (C.I. 62,045) which has previously been dissolved in water. The liquor is then made up to 1,500 liters with water. The liquor is heated up to boiling point in about fifteen minutes and left at boiling temperature for one hour. A pale blue dyeing is obtained which is just as beautiful and bright as on a previously bleached material.

## EXAMPLE 10

About 2,250 liters of water is placed in an alloyed steel cheese dyeing machine having a capacity of about 2,500 liters of liquor, the material carrier with 250 kg. of pre-cleaned woolen yarn in the form of cheeses is introduced and the circulation pump is switched on, in order to expel the bulk of the air from the cheeses. Then 0.6 kg. of ethylenediaminetetracetic acid, 1.2 kg. of sodium tripolyphosphate and 30 liters of a stock bleaching solution according to Example 9 are added to the liquor, the liquor is heated up to about 50° C., 25 kg. of anhydrous sodium sulfate and 20 kg. of ammonium acetate are added and the whole is made up to 2,500 liters with water. 375 g. of the dye C.I. Acid Blue 90 (C.I. 42,655) is dissolved in water and added to the liquor. The whole is heated to boiling temperature within twenty to thirty minutes, kept at this temperature for another forty to forty-five minutes, 3.7 liters of 60% acetic acid is added and dyeing is continued at the boiling point for another twenty to thirty minutes. The material is then rinsed in the usual way. A pale blue dyeing is obtained which is just as beautiful and bright as on previously bleached material.

10

The exhausted liquor may be appropriately replenished with active oxygen, i.e. with the stock bleaching solution according to Example 9, dye and other additives and used again for one or more further dyeing batches.

## EXAMPLE 11

The procedure of Example 10 is followed with the difference that 12 kg. of concentrated sulfuric acid is added to the liquor instead of 20 kg. of ammonium acetate, and 250 g. of C.I. Acid Blue 45 (C.I. 63,010) is used instead of C.I. Acid Blue 90.

## EXAMPLE 12

About 1,800 liters of water are placed in an alloyed steel suspension machine which will hold 2,000 liters of liquor and 0.45 kg. of sodium pyrophosphate, 0.24 kg. of ethylenediaminetetracetic acid and 16.5 liters of a stock bleaching solution formed from

	Parts
35% hydrogen peroxide -----	60
Water -----	35
10% sulfuric acid -----	2
Methyl formate -----	3

is dissolved therein. 1.5 kg. of 60% acetic acid and 0.5 kg. of the sodium salt of the acid sulfuric acid ester of an adduct of 1 mole of sperm oil alcohol and 80 moles of ethylene oxide are added and the whole made up to 2,000 liters with water. 200 g. of the dye in the form of its 1:2 chromium complex used in Example 5 is dissolved in water and added to the liquor and while the latter is being circulated, the material carrier carrying 100 kg. of unbleached pre-cleaned woolen yarn is introduced into the liquor. The liquor is heated to boiling temperature in forty to forty-five minutes and dyeing is carried out for another forty to forty-five minutes at the boiling temperature. The material is then rinsed with water in the usual way. A pale blue dyeing is obtained on the woolen yarn which is just as bright as on previously bleached yarn.

## EXAMPLE 13

100 kg. of pre-cleaned woolen yarn is chlorinated in the following way in an alloyed steel suspension machine which will hold 1,500 liters of liquor.

Prewetting is carried out for about ten minutes with 0.2 kg. of nonylphenol octaglycol ether in about 1,500 liters of cold water at 10° to 20° C. The material carrier is then withdrawn, 10 kg. of anhydrous sodium sulfate is dissolved in the wetting liquor, then a previously prepared solution of 2.5 kg. of anhydrous tetrasodium pyrophosphate and 4 kg. of potassium dichloroisocyanate in about 50 to 60 liters of water is added to the liquor which is then adjusted to a pH value of about 5 with acetic acid. The material carrier is then again introduced and the yarn is chlorinated at 10° to 20° C. for thirty to sixty minutes with the circulation pump running. If the active chlorine present is absorbed too slowly by the wool, the temperature may be raised to 25° to 30° C. for ten to fifteen minutes toward the end of the chlorination.

Then 0.675 kg. of sodium tripolyphosphate, 0.27 kg. of ethylenediaminetetracetic acid, 8 kg. of ammonium acetate, 15 liters of 35% hydrogen peroxide, 2.3 liters of diethylformamide and 3.5 liters of 10% sulfuric acid are added to the same liquor. Heating up of the liquor is then commenced and an aqueous solution of 50 g. of C.I. Acid Blue 59 (C.I. 50,315) is added at once. The liquor is heated up to boiling temperature in thirty minutes and left at heating temperature for forty to forty-five minutes. Then 1.5 liters of 60% acetic acid is added and dyeing is completed in another twenty to thirty minutes. The dyed yarn is rinsed in the usual way with water and the material carrier is removed from the machine.

A non-felted, creaseproof yarn having a pale blue dyeing where brightness is equivalent to that of a dyeing on sepa-

rately bleached yarn is thus obtained in one and the same liquor.

## EXAMPLE 14

About 900 liters of water is placed in an alloyed steel winch dyeing machine having a liquor capacity of 1,000 liters and 0.75 liter of 60% acetic acid, 1 kg. of ammonium sulfate and 125 g. of the sodium salt of the acid sulfuric acid ester of an adduct of 1 mole of sperm oil alcohol and 80 moles of ethylene oxide are dissolved therein. 0.15 kg. of sodium pyrophosphate, 0.135 kg. of ethylenediaminetetracetic acid and 8 liters of a stock bleaching solution consisting of:

	Parts
35% hydrogen peroxide -----	65
Diethylformamide -----	10
10% sulfuric acid -----	15
Water -----	10

are also added to the liquor. Finally 50 g. of the dye used in Example 7 is dissolved in water and added to the liquor and the liquor is made up to 1,000 liters with water. 50 kg. of unbleached precleaned woolen piece goods is introduced into the liquor, ten minutes is allowed to elapse to wet the goods, and the liquor is heated to boiling temperature within forty to forty-five minutes and left at boiling temperature for another forty to forty-five minutes. The liquor is then drained off and the good are rinsed in the usual way. A beautiful bright pale grey dyeing is obtained on the goods.

I claim:

1. A process for simultaneously dyeing and bleaching proteinaceous fibers in an aqueous liquor under non-alkaline conditions, which comprises treating the fibers at an elevated temperature as required for dyeing wool in an aqueous liquor which has a pH-value of 1 to 7 and which contains (a) an acid dye capable of dyeing wool and resistant to peroxides, (b) performic acid, said performic acid being formed by reaction of hydrogen peroxide with a compound selected from the group consisting of compounds capable of splitting off formaldehyde under the reaction conditions, low molecular weight formic acid alkanol esters and low molecular weight formamides, and (c) at least one oxygen stabilizer selected from the group consisting of magnesium phosphate, alkali metal polyphosphates and complex-forming amino-polycarboxylic acids

and their ammonium, alkali metal and alkaline earth metal salts, the amount of active oxygen initially available for said treatment being 0.2 to 10 g./l. and the amount of said oxygen stabilizer being about 0.1 to 1 times the weight of active oxygen initially available when using said amino-polycarboxylic acids, their salts and mixtures as the stabilizer and about 2 to 30 times the weight of active oxygen initially available when using only a phosphate stabilizer.

2. A process according to claim 1 wherein wool is simultaneously dyed and bleached.

3. A process according to claim 1 wherein performic acid is formed from compounds capable of splitting off formaldehyde and ammonia.

4. A process according to claim 1 wherein performic acid is formed from low molecular weight formamide.

5. A process according to claim 1 wherein performic acid is formed by reacting hydrogen peroxide with hexamethylenetetramide.

6. A process according to claim 1 wherein performic acid is formed by reacting hydrogen peroxide with formamide.

7. A process according to claim 1 wherein performic acid is formed by reacting hydrogen peroxide with dimethylformamide.

8. A process according to claim 1 wherein performic acid is formed by reacting hydrogen peroxide with hydroxymethane sulfonate.

9. A process according to claim 1 wherein performic acid is formed by reacting hydrogen peroxide with iminobis-methane sulfonate.

## References Cited

## UNITED STATES PATENTS

3,363,970 1/1968 Schaffner ----- 8-19  
3,374,177 3/1968 Schmidt et al. ----- 252-186

## FOREIGN PATENTS

1,032,260 6/1966 Great Britain.

NORMAN G. TORCHIN, Primary Examiner

J. E. CALLAGHAN, Assistant Examiner

U.S. Cl. X.R.

8-54

PO-1050  
(5/69)

UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,551,087 Dated December 29, 1970

Inventor(s) Oswald Schmidt

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 9, in the heading, "1,469,607" should read -- 1,469,609 --.

Column 3, line 75, delete the entire line.

Column 4, line 40, "alnaline" should read -- alkaline --.

Column 6, line 52, "in" should read -- is --.

Signed and sealed this 4th day of May 1971.

(SEAL)  
Attest:

EDWARD M. FLETCHER, JR.  
Attesting Officer

WILLIAM E. SCHUYLER,  
Commissioner of Patent

L