Patented May 8, 1951

2,552,404

# UNITED STATES PATENT OFFICE

2,552,404

## PROCESS FOR DYEING ANIMAL AND OTHER FIBERS HAVING SIMILAR PROPERTIES

Richard Casty, Allschwil, Switzerland, assignor to Ciba Limited, Basel, Switzerland, a Swiss firm

No Drawing. Application June 16, 1947, Serial No. 755,012. In Switzerland June 28, 1946

11 Claims. (Cl. 8—29)

1

According to this invention animal fibers and other fibers, which have dyeing properties similar to those of animal fibers, are dyed in an especially simple manner by bringing the fibers impregnated with the dyestuff solution into sudden contact with a heated acidic solution.

As animal fibers which can be dyed by the present process there come into consideration, for example, silk fibers and especially wool fibers. Fibers which have dyeing properties similar to those of animal fibers are, for example, the artificial fibers consisting mainly of casein and known under the names "Thiolan" and "Lanital." There also come into consideration artificial silk fibers and staple fibers of cellulose or cellulose derivatives which have been animalized by the addition of suitable substances, and also other fibers which have been animalized by a special treatment.

In the present process such fibers are first soaked or impregnated with a dyestuff solution. This treatment may be carried out in known manner by immersing the fibers in question in a dyestuff solution, and advantageously subsequently squeezing the fibers. For the purposes of the present process the period of this treatment need only be long enough to bring about a uniform impregnation of the fibrous material. It is not necessary or advantageous to prolong the period of treatment beyond this point. When materials of normal absorptive capacity are used, for example, in the case of fabrics which have been desized and advantageously also washed and dried, the impregnation is carried on for a very short time and may, for example, be carried out on a padding machine.

The concentration of the dyestuff solution must, of course, be so chosen that the desired quantity of dyestuff remains on the fiber after the effect of the squeezing operation has been taken into account. In some cases this necessitates relatively high concentrations of dyestuff in the impregnating baths, and in the case of some dyestuffs this can only be achieved in a medium which is substantially non-acidic, for example, one which is approximately neutral or alkaline, and is advantageously at most weakly alkaline. The use of a non-acidic impregnating bath generally has the further advantage that

2

absorption of the dyestuff in the bath is avoided to a considerable extent.

In some cases the temperature of the impregnating bath plays a subsidiary part and may be chosen, for example, with regard to the properties of solubility of the dyestuff used, within wide limits, for instance, between 20° C. and 95° C. In a few cases, however, there are differences in the yield of the dyeing, so that it is of advantage in the case of any particular dyestuff and fibrous material to determine by experiment the most favorable temperature for the impregnating bath. In many cases a temperature of about 75° C. gives good results.

Some degree of swelling of the fibrous material, which can be favoured, for example, by increasing the temperature of the impregnating bath, and also thorough penetration of the fibrous material, which can be assisted, for example, by the addition of certain wetting agents, have a favorable effect in many cases. It must, however, be borne in mind that some wetting agents, for instance, those of the type of alkylnaphthalene sulfonic acids, retard or even prevent fixation of the dyestuff.

In the case of dyestuffs of insufficient solubility it may be of assistance in most cases to add solution promoters such as urea, thiodiglycol or glycol monoethyl ether, to choose especially easily soluble dyestuff salts, for example, lithium salts, to increase the temperature of the dyestuff solution or to use a combination of such expedients. In some cases a good effect is obtained by adding to the impregnating bath a thickening agent such as tragacanth mucilage or a water-soluble cellulose ether, especially cellulose glycollic acid ether, and advantageously only in quantities such that the bath is still thinly liquid. For example, there may be used, per liter, 50–100 grams of tragacanth mucilage of 6 per cent. strength or of a solution of 10 per cent. strength of cellulose glycollic acid ether.

Other additions are of advantage in the case of certain dyestuffs. Thus, for example, the addition of formaldehyde-sulfoxylates is of advantage with impregnating baths which contain sensitive ester salts of leuco-compounds of vat dyestuffs.

In the present process practically all dyestuffs can be used which possess an affinity for animal

fibers, for example, the usual acid dyestuffs, and also substantive (direct dyeing) dyestuffs and especially dyestuffs which require a special after-treatment, for example, chrome dyestuffs and ester salts of leuco-compounds of vat dyestuffs. In the case of dyestuffs of all kinds requiring an after-treatment it is, of course, necessary to associate with the present dyeing process an appropriate after-treatment.

The fibers impregnated in the above manner with a dyestuff solution are then brought into sudden contact with a heated acidic solution. As the acidic solution there may be used an aqueous solution of sulfuric acid such as is customarily used in dyeing wool and having a content of about 0.5–30 grams, and advantageously about 1 gram, of sulfuric acid per liter of liquor. Instead of sulfuric acid other acids may be used in many cases, for example, formic acid or oxalic acid, and with special advantage in the case of dyestuffs which are sensitive to mineral acids. It is often of advantage to use mixtures of different acids, for example, mixtures of sulfuric acid and formic acid, as in the case of sulfuric acid leucoesters of indigo. In many cases it appears to be of advantage to use acidic solutions which have a pH value corresponding to the optimum speed of fixation of the fibers in question, provided they do neither unfavorably influence the dyestuff, nor for instance, produce a skittery dyeing by too rapid fixation. In this connection the desired pH value may be attained by using an acid salt alone or by the joint use of such a salt in any desired manner, for example, by means of monobasic salts of ortho-phosphoric acid. This is indicated, more especially, in the case of dyestuffs which become fixed very rapidly, such as the sulfuric acid esters of many leuco-compounds of vat dyestuffs. It is occasionally of advantage to buffer the acids used by means of their own salts, for example, sulfuric acid by means of its own salts, for example, sulfuric acid by means of sodium sulfate. Quite generally, in order to obtain the best results, the concentration and nature of the acidic solution and also of the buffer substances, when used, should be chosen according to the character and quantity of the dyestuff used. The optimum conditions for each case can be determined by preliminary tests.

An addition of anion-active or cation-active substances to the acidic bath is generally not desirable and may even be harmful. On the other hand, some non-ionisable wetting agents may in certain cases have a favorable influence. As such wetting agents there may be mentioned, for example, condensation products of alcohols of high molecular weight with ethylene oxide, which as is known contain polyglycol ether residues.

In the process of the invention it is of advantage to use strongly heated acidic solutions, that is to say, those which are heated at above 80° C., for example, boiling solutions.

The period during which the fibers impregnated with the dyestuff solution are treated in the heated acidic bath need generally be only very short, for example, ½ to 10 minutes. In many cases a period of treatment of 2–7 minutes suffices. The duration of the treatment depends mainly on the dyestuff and on the intensity of the dyeing.

The present process enables the dyeing of animal fibers, especially wool, to be carried out in a continuous manner, since the impregnation of the fibers and also the operation of bringing the impregnated fibers into contact with the acidic solution require only a short time. Thus, for example, the fibers in the form of a woven fabric, knitted fabric, yarn or combed material or other loose form may be passed through a padding machine, advantageously provided with squeezing rollers disposed beneath the level of the liquid, and then passed directly, or after an intermediate travel through the air, in a roller vat or a similar apparatus through the acidic bath. Care must naturally be taken to keep the pH value of the acidic bath constantly at the optimum ascertained for the particular dyeing operation by renewing the acid and, when necessary, the buffer salt.

The impregnated goods may be dried before the acidic treatment. In some cases somewhat stronger dyeings are obtained in this manner.

The fact that the present process succeeds is surprising in many respects. It could not be expected that the fixation of the dyestuff would be possible in so short a time. Moreover, extraordinary inequality in the dyeing result was to have been feared, and finally it would have been supposed that relatively large, and in some cases incalculable and uncontrollable, quantities of the dyestuff would be washed into the acidic bath. The process need not necessarily be carried out in a continuous manner. The fibrous material may be treated in a non-continuous manner, provided that the fibers which have been treated in the first step of the process are given a "shock" treatment with a heated acidic solution.

After the acidic treatment, the goods dyed by the present process may be immediately rinsed and finished in the usual manner, provided that the dyestuff used does not necessitate any special after-treatment.

When dyestuffs are used in the process which require a special after-treatment, the latter treatment may be carried out in the known manner immediately following the present dyeing process. However, it is of advantage in many cases to carry out such after-treatment in a correspondingly shortened manner so that it can be incorporated in the continuous dyeing process. Thus, for example, chrome dyestuffs, principally those which are resistant to an excess of bichromate, and also ester salts of leuco compounds of vat dyestuffs, may be developed by passing the goods, immediately after leaving the acidic bath, into a chroming bath which is advantageously relatively strongly heated. The latter bath may contain, for example, up to 30 grams, and advantageously about 5 to 10 grams, of sulfuric acid per liter and also a suitable quantity of potassium bichromate or sodium bichromate, for example, 0.5 to about 3 grams per liter. In certain cases the sulfuric acid may be replaced by another acid, for example, formic acid. Sometimes it suffices to use alkali bichromate baths containing no acid addition. In the case of after-chromable dyestuffs it is of advantage to use a boiling bath, while in the case of ester salts of leuco-compounds of vat dyestuffs a temperature of 85–90° C. often gives better results. Under these circumstances the chroming or oxidation is generally complete after about 15–60 seconds.

The goods after-treated in this manner are then advantageously rinsed, and treated in a suitable bath which has a neutralizing action and simultaneously dissolves the excess of chromium compounds out of the fibers. As a neutralizing bath any bath having an alkaline reaction may

be used, and which may contain as an alkali, for example, sodium carbonate, ammonia, borax, secondary or tertiary sodium phosphate or even ammonium carbonate. When a relatively high temperature is used, for example 80° C., a period of treatment of about 2 minutes suffices in most cases, so that injury to the wool is avoided by the short duration of the treatment, especially when weak alkalies such as secondary sodium phosphate are used.

If the after-treatment above described has undesired results, for example, over-oxidation of the dyestuff used or a residual dyeing of the wool due to the excess of chromium, it may be of advantage to impregnate the fibers first with a chromate solution which is at most weakly acid, for example, a bichromate solution, and then to bring them into an acid developing bath. For example, after leaving the acidic bath which serves to fix the dyestuff, the fibers may be powerfully squeezed, and then padded or slopped on a padding machine having a smaller squeezing effect with a concentrated, advantageously somewhat thickened, bichromate solution. By suitably adjusting the two squeezing effects and the concentration of the chromate solution it is possible to ensure that only the final necessary quantity, possibly increased by a certain margin of safety, is supplied to the fibers. Another method of charging a travelling web of the goods with chromium is to spray it with a chromate solution in a finely atomized state. Furthermore, by immersion for some time in a chromate solution, followed, for example, by a squeezing operation the goods may be charged with chromium. In this case, however, the quantity of bichromate taken up depends very closely on the period of immersion, the concentration, the temperature and the pH value of the chroming bath.

The fibers thus charged with chromic salts and dyestuff may then be introduced directly into an acid bath, which in the case of ester salts of leuco-compounds of vat dyestuffs may contain, for example, 2 to 50 grams, and advantageously 5 to 10 grams, of sulfuric acid per liter. It is frequently of advantage to add to the bath a small quantity, for example, 0.5 to 2 grams per liter, of ammonium thiocyanate. Other substances such as oxalic acid or sulfites may in some cases also yield good results. A temperature of about 90° C. is usually advantageous.

For the after-treatment of chrome dyestuffs it is often of advantage to work with boiling but relatively weakly acid baths, for example, formic acid or acetic acid baths. In such cases excess sulfuric acid originating from the boiling fixing bath may be neutralized by the addition, for example, of sodium formate or sodium acetate. An addition of ammonium thiocyanate is also frequently of advantage in this case. These additions of buffer salts and thiocyanates may also be made to the preceding chrome-charging bath. It is then frequently unnecessary to make additions to the hot after-treatment bath.

The duration of the treatment in the latter developing bath depends on the nature and quantity of the dyestuff used. It generally ranges from 1 to 7 minutes, and only in exceptional cases transgresses these limits.

By the above described procedure of separating the operations of charging with chromium and chroming proper no excess or only a slight excess of bichromate is applied to the fibers. The warm alkaline bath for removing excess of chromium can therefore be dispensed with. Only when large quantities of sulfuric acid are used, such as are necessary for the oxidation of sulfuric acid ester salts of leuco-compounds of vat dyestuffs, is it advisable to apply a cold alkaline after-treatment with, for example, 1 gram of anhydrous sodium carbonate per liter.

An alternative method of oxidizing dyeings of ester salts of leuco-compounds of vat dyestuffs is to pass the goods at 85–90° C. for about 15–30 seconds through a bath containing, per liter, for example:

50 grams of concentrated sulfuric acid
30 grams of sodium chlorate and
0.3 gram of ammonium vanadate.

After the completion of the dyeing process including any necessary after-treatments, the goods may be rinsed and finished in the usual manner.

In many cases it is of advantage to add to the rinsing and neutralizing baths washing agents of natural or synthetic character, which may serve to remove precipitated dyestuff particles on the surface.

In order to complete the treatment the goods, which have been thus dyed, may again be rinsed in the usual manner with cold, for example, running, water.

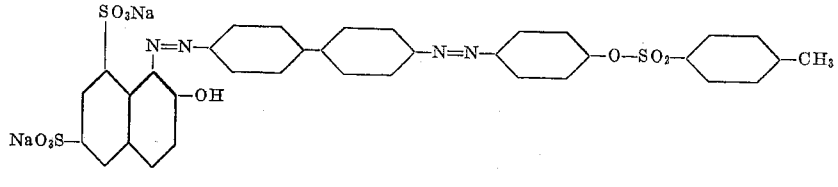
For carrying out the present process the continuous-dyeing machines known in the cotton dyeing industry may be used, in which case the troughs or vats should be made of acid-resistant material, for example, acid-resistant steel, in view of the acid character of the fixing bath and, as the case may be, of the after-treatment bath. Slubbing may be treated on a machine which is similar in construction to the known back-washing machine, and loose wool on a type of Leviathan washing machine, and so on. The period of travel of the goods through the treatment baths is advantageously at or over the minimum at which a, if desired, very small but constant concentration of the dyestuff in the fixing bath is adjusted and the desired reaction in any after-treatment bath is completed.

The following examples illustrate the invention.

*Example 1*

Dry wool piece goods of light quality are impregnated at 80° C. on a padding machine or an impregnating machine with a solution containing, per liter,

40 grams of the dyestuff of the formula



40 cc. of thiodiglycol and
2 grams of the sodium salt of benzyl-μ-heptadecyl-benzimidazole disulfonic acid.

The goods, after being impregnated and squeezed, are passed immediately, or after passage through the air, through a roller vat of acid-resistant material which contains a boiling solution of 5 grams of concentrated sulfuric acid per liter. The goods are passed through the roller vat in an extended condition. The duration of the passage is 3–4 minutes. The goods are then rinsed in warm water, advantageously with the addition, per liter of rinsing liquor, of 1 gram of the sodium salt of benzyl-μ-heptadecyl-benzimidazole disulfonic acid or of a similar acid-resistant washing agent. The washing and rinsing may be carried out in a continuous manner on a broad washing machine or a skein washing machine. The goods are then dried. A powerful red dyeing is obtained.

*Example 2*

Loose washed wool is immersed in a bath at a temperature of 80° C., which contains, per liter,

60 grams of Cloth Fast Black B in the form of the concentrated powder (Colour Index No. 307)
60 cc. of thiodiglycol and
2 grams of the sodium salt of benzyl-μ-heptadecyl-benzimidazole disulfonic acid,

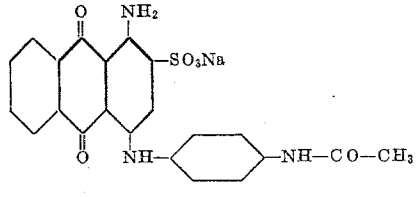
until it is completely wetted. The wool is then freed from excess of the dyestuff solution by squeezing, centrifuging or suction, and passed in the course of 8 minutes through a boiling bath containing per liter,

7 cc. of formic acid and
3 cc. of a solution of about 20 per cent. strength of the condensation product of about 20 molecular proportions of ethylene oxide with 1 molecular proportion of an ordinary commercial mixture of octadecyl alcohol and cetyl alcohol.

The material is then treated in warm water, which may have an addition of an acid-resistant washing agent, rinsed in the cold, and dried. A black dyeing is obtained.

*Example 3*

Slubbing of wool is dyed in a manner similar to that described in Example 1. In the housing of an impregnating padding machine is placed a solution containing 8 grams of the dyestuff of the formula:




and 2 grams of the sodium salt of benzyl-μ-heptadecyl-benzimidazole disulfonic acid at a temperature of 80° C. The combed material is passed through the padding machine and then brought into a boiling bath containing 1 gram of concentrated sulfuric acid and 4 grams of crystalline sodium sulfate, per liter. The material is treated in this bath at the boiling temperature for 5 minutes, and then rinsed in a subsequent bath with blood-warm which may contain, per liter, 1 gram of the sodium salt of benzyl-μ-heptadecyl-benzimidazole disulfonic acid. The material is then



thoroughly rinsed in cold running water and dried. A blue dyeing is obtained.

*Example 4*

The procedure is the same as that described in Example 1, except that the impregnating liquor is at a temperature of 70° C. and contains, per liter,

30 grams of Orange II (Colour Index 151) and
2 grams of the sodium salt of benzyl-μ-heptadecyl-benzimidazole disulfonic acid.

The impregnated material is then passed in the course of 5 minutes through a boiling fixing bath which contains, per liter, 1 gram of concentrated sulfuric acid. The material is then rinsed as described in Example 1. A powerful orange dyeing is obtained.

*Example 5*

The procedure is the same as that described in Example 1, except that the impregnating liquor is at a temperature of 90° C. and contains, per liter,

40 grams of Acid Black HA in the form of the concentrated dyestuff powder (Colour Index 246),
120 cc. of thiodiglycol and
2 grams of the sodium salt of benzyl-μ-heptadecyl-benzimidazole disulfonic acid.

The subsequent boiling fixing bath, contains, per liter,

1 gram of concentrated sulfuric acid
2 grams of crystalline sodium sulfate and
3 cc. of the ethylene oxide condensation product mentioned in Example 2.

The period of the passage is 7 minutes. The material is then rinsed, advantageously with the addition of the sodium salt of benzyl-μ-heptadecyl-benzimidazole disulfonic acid, and dried. A black dyeing is obtained.

*Example 6*

The procedure is the same as that described in Example 1, except that the impregnating bath, used at 80° C., contains per liter,

25 grams of Chlorantin Red 8BN in the form of the concentrated dyestuff powder (Colour Index 436),
20 cc. of thiodiglycol and
2 grams of the sodium salt of benzyl-μ-heptadecyl-benzimidazole disulfonic acid.

The material is then passed in an extended condition through a boiling fixing bath which contains, per liter,

1 gram of concentrated sulfuric acid, and
1.5 cc. of the ethylene oxide condensation product mentioned in Example 2.

The period of passage is 7 minutes. The material is then rinsed, advantageously with the addition of an acid-resistant washing material, again rinsed in water, and dried. A powerful wine-red dyeing is obtained.

*Example 7*

Slubbing of wool is treated in the manner described in Example 3, except that the impregnating liquor, used at 80° C., contains, per liter,

40 grams of Direct Fast Yellow FF (Colour Index No. 814) and
2 grams of the sodium salt of benzyl-μ-heptadecyl-benzimidazole disulfonic acid.

The material is then passed through a boiling fixing bath, which contains, per liter, 1 gram of concentrated sulfuric acid, 16 grams of crystalline sodium sulfate and 1.5 cc. of the ethylene oxide condensation product mentioned in Example 2. The period of passage is 6 minutes. The material is then rinsed and dried as described in the foregoing examples. A yellow dyeing is obtained.

*Example 8*

Dry wool piece goods of light quality are impregnated on the padding machine or on an impregnating machine at 80° C. with a solution containing, per liter, 15 grams of the complex chromium compound of the dystuff obtained from diazotized 1-hdyroxy-2-aminobenzene - 4 - sulfamide and 1-(3'-sulfamido) - phenyl-3-methyl-5-pyrazolone, in the form of a concentrated dyestuff powder, and 2 grams of the sodium salt of benzyl - $\mu$ - heptadecyl-benzimidazole-disulfonic acid. The goods, after being impregnated and squeezed, are passed immediately, or after passage through the air, through a roller vat of acid-resistant material which contains a boiling solution of 1 gram of concentrated sulfuric acid and 2 cubic centimeters of the ethylene oxide condensation product mentioned in Example 2. The period of passage is 6 minutes. After this, the goods are thoroughly rinsed with warm water, advantageously with the addition of an acid-resistant washing agent, rinsed again in cold water, and dried. An orange dyeing is thus obtained.

*Example 9*

Dry piece goods of wool are impregnated on a padding machine or in an impregnating machine permitting of the introduction of the goods with a reduced air content, with a solution at a temperature of 80° C. containing, per liter,

12 grams of the dyestuff obtainable from 2:6-dichloro-benzaldehyde and 2 molecular proportions of ortho-cresotinic acid followed by oxidation, as described in Example 1 of German Specification No. 199,943, and
2 grams of the sodium salt of benzyl-$\mu$-heptadecyl-benzimidazole disulfonic acid.

The goods are passed in an extended condition through a boiling fixing bath, which contains, per liter, 2 cc. of formic acid of 85 per cent. strength and 4 grams of sodium formate. The period of passage is 6 minutes. The material is then squeezed and immediately passed, advantageously while still in the extended condition, into a boiling chroming bath. The latter bath contains, per liter, 2 grams of sulfuric acid and 1 gram of potassium bichromate or sodium bichromate. The period of passage is 45 seconds. The goods are then rinsed in warm water. In order to remove the yellow coloration due to the chroming the goods are passed into a bath at 80° C. which contains, per liter, 10 grams of crystalline disodium phosphate and 1 gram of the sodium salt of benzyl-$\mu$-heptadecyl-benzimidazole disulfonic acid. The period of passage is 2 minutes. The goods are then thoroughly rinsed. A pure blue dyeing is obtained.

*Example 10*

Washed loose wool is immersed until completely wetted in a bath at 80° C. which contains, per liter, 10 grams of the dyestuff obtainable from diazotized 4 - chloro-2-amino-1-hydroxybenzene-6-sulfonic acid and 1-phenyl-3-methyl-5-pyrazolone. The wool is freed from excess of the dyestuff solution by squeezing, centrifuging or suction, and then passed in the course of 6 minutes through a boiling bath which contains per liter 1 gram of concentrated sulfuric acid and 2 grams of crystalline sodium sulfate. It is then squeezed, and sprayed with a solution which contains, per liter, 30 grams of potassium bichromate or sodium bichromate and 250 grams of crystalline sodium acetate. The apparatus is so arranged that the quantity of the sprayed solution taken up by the loose wool amounts to 50 per cent. of the dry weight of the latter. In this manner the wool is charged with 1.5 per cent. of bichromate and a sufficient quantity of buffer salt to neutralize the excess sulfuric acid. The wool is then passed for 7 minutes through a bath of boiling water. It is then rinsed in the warm and

*Example 11*

An impregnating bath is prepared, which contains, per liter,

25 grams of the dyestuff from diazotized 4-chloro-2-amino - 1 - hydroxybenzene and 1:8-dihydroxy-naphthalene-3:6-disulfonic acid,
20 cc. of thiodiglycol and

in the cold, and dried. A red dyeing is obtained.
2 grams of the sodium salt of benzyl-$\mu$-heptadecyl-benzimidazole disulfonic acid.

A wool fabric is treated on a padding machine in this bath at 80° C., and squeezed until its content of moisture is 100 per cent. The fabric is then treated for 7 minutes at the boiling temperature in a bath which contains, per liter, 2 grams of concentrated sulfuric acid and 2 cc. of the ethylene oxide condensation product mentioned in Example 2. After rigorous squeezing the material is padded with a thickened bichromate bath which contains per liter 26 grams of sodium bichromate and 100 grams of a solution of 10 per cent. strength of cellulose glycol ether. The apparatus is so adjusted that the increase in weight of the wet goods in the padding machine, as compared with the previous squeezing machine, amounts to 80 per cent. on the dry weight of the goods. In the case of different squeezing conditions the concentration of bichromate in the padding bath must be proportionately changed. The material is then passed into a bath which contains, per liter, ½ cc. of formic acid of 85 per cent strength, 1 gram of sodium formate and 1 gram of ammonium thiocyanate. The wool is treated in this bath for 7 minutes at the boiling temperature, and is then rinsed and finished in the usual manner. A dark blue dyeing is obtained.

*Example 12*

Loose wool is impregnated at 70° C. with a solution which contains, per liter,

25 grams of the sodium salt of the sulfuric acid leuco-ester of 6:6'-diethoxy-thioindigo,
25 grams of the sodium salt of the sulfuric acid leuco-ester of 4:4' - dimethyl - 6:6' - dichloro-thioindigo,
50 cc. of thiodiglycol,
15 grams of sodium formaldehyde sulfoxylate and
2 grams of the sodium salt of benzyl-$\mu$-heptadecyl-benzimidazole-disulfonic acid.

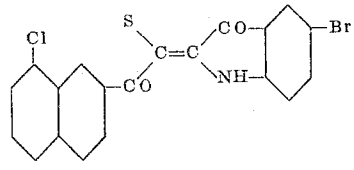
The material is then passed in the course of 7 minutes through a boiling bath which contains per liter, 1 cc. of formic acid of 85 per cent. strength, 4 grams of sodium formate and 3 cc. of the ethylene oxide condensation product mentioned in Example 2. The wool is then passed

into an oxidizing bath at 90° C. which contains, per liter, 10 grams of concentrated sulfuric acid and 1 gram of sodium bichromate. The period of passage is 1 minute. The material is then rinsed in the warm, and passed in the course of 5 minutes through a neutralizing bath. The latter, which is at a temperature of 60° C., contains 10 grams of ammonium carbonate and 1 gram of the sodium salt of benzyl-μ-heptadecyl-benzimidazole-sulfonic acid, per liter. The material is then thoroughly rinsed and dried. A scarlet dyeing is obtained.

*Example 13*

Dry wool muslin is impregnated on a three-roller padding machine or in a modern impregnating machine permitting of the introduction of the goods with a reduced air content, with a solution at 75° C. which contains per liter,

8 grams of the sodium salt of the sulfuric acid leuco-ester of the dyestuff of the formula



10 grams of sodium formaldehyde sulfoxylate and
2 grams of the sodium salt of benzyl-μ-heptadecyl-benzimidazole disulfonic acid.

The goods are then passed immediately into a roller vat composed of acid-resistant material, which contains, an approximately boiling solution of 10 grams of mono-ammonium phosphate and 1 cc. of the ethylene oxide condensation product mentioned in Example 2, per liter. The period of treatment in this bath is 3 minutes.

The squeezing goods are then padded in the manner described in Example 10 with a thickened solution containing per liter,

9 grams of potassium bichromate or sodium bichromate,
9 grams of ammonium thiocyanate and
100 grams of a solution of 10 per cent strength of cellulose glycol ether.

The goods are then treated for 2 minutes at 90° C. in a bath containing 10 grams of concentrated sulfuric acid per liter. The goods are then rinsed in the warm, if desired with the addition of an acid-resistant washing agent, then neutralized in the cold with a solution containing 1 gram of anhydrous sodium carbonate per liter, and again rinsed, and dried. A grey dyeing is obtained.

*Example 14*

A wool fabric is treated on the padding machine at 70° C. in a bath which contains per liter,

10 grams of the sodium salt of the sulfuric acid ester of the leuco compound of 4:7'-dimethyl-6:6'-dichloro-thioindigo
10 grams of sodium formaldehyde sulfoxylate
100 grams of a solution of 10 per cent strength of cellulose glycol ether and
2 grams of the sodim salt of benzyl-μ-heptadecyl-benzimidazole disulfonic acid.

The goods are then treated for 5 minutes at the boiling temperature in a bath containing per liter, 15 grams of monoammonium phosphate and 1 cc. of the ethylene oxide condensation product described in Example 2. The material is then padded in the manner described in Example 10 in a bath containing, per liter, 13 grams of sodium bichromate and 100 grams of a solution of 10 per cent strength of cellulose glycol ether, and the goods are then passed into a bath which contains, per liter, 10 grams of concentrated sulfuric acid and ½ gram of ammonium thiocyanate. In the latter bath the goods are treated for 4 minutes at 90° C. The goods are then rinsed in the warm, neutralized in the cold with a dilute solution of sodium carbonate, and again rinsed, and dried. A fast pink dyeing is obtained.

*Example 15*

Wool piece goods are treated in accordance with the procedure described in Example 1. The impregnated liquor used at 70° C. contains per liter;

160 grams of the sodium salt of the sulfuric acid leuco-ester of indigo
20 grams of sodium formaldehyde sulfoxylate and
2 grams of the sodium salt of benzyl-μ-heptadecyl-benzimidazole disulfonic acid.

The succeeding fixing bath contains an approximately boiling solution containing per liter, 1 gram of concentrated sulfuric acid, 1 cc. of formic acid of 85 per cent. strength and 3 cc. of the ethylene oxide condensation product mentioned in Example 2. The period of passage is 7 minutes. The goods are then padded in the manner described in Example 11 in a thickened solution which contains per liter, 35 grams of potassium bichromate or sodium bichromate and 100 grams of a solution of 10 per cent. strength of cellulose glycol ether. The goods are then passed in the course of 3 minutes through a bath at 80–90° C. which contains, per liter, 8 grams of concentrated sulfuric acid and 2 grams of ammonium thiocyanate. The goods are then rinsed in warm water which contains 1 gram of the sodium salt of benzyl-μ-heptadecyl-benzimidazole disulfonic acid per liter. The goods are then neutralized in the cold with a solution containing 1 gram of anhydrous sodium carbonate per liter, rinsed, and dried. A powerful deep blue dyeing is obtained.

*Example 16*

Slubbing of wool is treated in the manner described in Example 3, except that the impregnating liquor, is used at 60° C., and contains, per liter,

30 grams of the sodium salt of the sulfuric acid leuco-ester of dimethoxy-dibenzanthrone,
10 grams of sodium formaldehyde sulfoxylate and
2 grams of the sodium salt of benzyl-μ-heptadecyl-benzimidazole disulfonic acid.

The succeeding boiling fixing bath contains, per liter, 1 cc. of formic acid, 8 grams of sodium formate and 5 cc. of the ethylene oxide condensation product mentioned in Example 2. The period of treatment is 6 minutes. The combed material is then passed into the oxidizing bath. The latter which is used at 90° C., contains per liter,

50 grams of concentrated sulfuric acid,
30 grams of sodium chlorate and
0.3 gram of ammonium vanadate.

The period of passage is 20 seconds. After being squeezed the goods are rinsed in the warm and then introduced into a cold neutralizing bath containing per liter, 2 grams of anhydrous sodium carbonate and, if desired 1 gram of the so-

dium salt of benzyl-$\mu$-heptadecyl-benzimidazole disulfonic acid. The goods are then thoroughly rinsed and dried. A green dyeing is obtained.

What I claim is:

1. A process for dyeing wool which comprises bringing wool impregnated with a solution of a dyestuff of the kind possessing affinity for wool due to the presence of acid groups in the dyestuff into sudden contact with an aqueous acidic solution, heated to about its boiling point, the acidity of which corresponds to that of a solution containing not more than 30 grams of $H_2SO_4$ in one liter of water, the said acidic solution being free from oxidizing agents and free from reducing agents harmful to the dyestuff, the whole dyeing operation being carried out under atmospheric pressure.

2. A process for dyeing wool which comprises bringing wool impregnated with a substantially non-acidic solution of a dyestuff of the kind possessing affinity for wool due to the presence of acid groups in the dyestuff into sudden contact with an aqueous acidic solution, heated to about its boiling point, the acidity of which corresponds to that of a solution containing not more than 30 grams of $H_2SO_4$ in one liter of water, the said acidic solution being free from oxidizing agents and free from reducing agents harmful to the dyestuff, the whole dyeing operation being carried out under atmospheric pressure.

3. A process for dyeing wool which comprises bringing wool impregnated with a substantially non-acidic solution of an acid wool dyestuff into sudden contact with an aqueous acidic solution, heated to about its boiling point, the acidity of which corresponds to that of a solution containing not more than 30 grams of $H_2SO_4$ in one liter of water, the said acidic solution being free from oxidizing agents and free from reducing agents harmful to the dyestuff, the whole dyeing operation being carried out under atmospheric pressure.

4. A process for dyeing wool which comprises bringing wool impregnated with a substantially non-acidic solution of a substantive dyestuff possessing acid groups into sudden contact with an aqueous acidic solution, heated to about its boiling point, the acidity of which corresponds to that of a solution containing not more than 30 grams of $H_2SO_4$ in one liter of water, the said acidic solution being free from oxidizing agents and free from reducing agents harmful to the dyestuff, the whole dyeing operation being carried out under atmospheric pressure.

5. A process for dyeing wool which comprises bringing wool impregnated with a substantially non-acidic solution of a sulfuric acid ester of a leuco vat dyestuff into sudden contact with an aqueous acidic solution, heated to about its boiling point, the acidity of which corresponds to that of a solution containing not more than 30 grams of $H_2SO_4$ in one liter of water, the said acidic solution being free from oxidizing and free from reducing agents harmful to the dyestuff, the whole dyeing operation being carried out under atmospheric pressure.

6. A process as claimed in claim 1, wherein the acidity of the aqueous acidic solution corresponds to that of a solution containing about 1 gram of $H_2SO_4$ in one liter of water.

7. A process as claimed in claim 2, wherein the acidity of the aqueous acidic solution corresponds to that of a solution containing about 1 gram of $H_2SO_4$ in one liter of water.

8. A process as claimed in claim 3, wherein the acidity of the aqueous acidic solution corresponds to that of a solution containing about 1 gram of $H_2SO_4$ in one liter of water.

9. A process as claimed in claim 4, wherein the acidity of the aqueous acidic solution corresponds to that of a solution containing about 1 gram of $H_2SO_4$ in one liter of water.

10. A process as claimed in claim 5, wherein the acidity of the aqueous acidic solution corresponds to that of a solution containing about 1 gram of $H_2SO_4$ in one liter of water.

11. A process for dyeing wool which comprises bringing wool impregnated with a substantially non-acidic solution of an acid wool dyestuff capable of being after-chromed into sudden contact with an aqueous acidic solution, heated to about its boiling point, the acidity of which corresponds to that of a solution containing about 1 gram of $H_2SO_4$ in one liter of water, the said acidic solution being free from oxidizing and free from reducing agents harmful to the dyestuff, then charging the wool with the required amount of a chromate solution and subjecting the wool to an acidic treatment for effecting the chroming reaction, the whole dyeing operation being carried out under atmospheric pressure.

RICHARD CASTY.

**REFERENCES CITED**

The following references are of record in the file of this patent:

UNITED STATES PATENTS

| Number | Name | Date |
|---|---|---|
| 1,575,958 | Bader | Mar. 9, 1926 |
| 1,850,551 | Jones | Mar. 22, 1932 |
| 2,095,600 | Graenacher | Oct. 12, 1937 |
| 2,387,200 | Walter | Oct. 16, 1945 |

OTHER REFERENCES

Amer. Dye. Reporter for Jan. 10, 1949, pp. P9, P26–P32.