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PERSULFATE AND HYPOCHLORITE TREATMENT OF DARK OR MEDIUM COLORED WOODS

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14 Claims

ABSTRACT OF THE DISCLOSURE

The invention relates to a process for imparting stabilised colour to wood and other ligno-cellulosic materials. In the process, the wood is treated with an oxidizing agent so as to produce therein light-stable products which stabilise the colour of the wood. Preferred details for the treatment of various materials are given.

The invention relates to a method of treating wood and other ligno-cellulosic materials so as to produce a stable colour resistant to changes due to photochemical action.

It has been found that many woods change colour on exposure to light and that this is due to photochemical activity. The change in colour is particularly rapid with freshly-exposed surfaces.

Attempts have been made in the past to overcome this problem by applying reducing agents to the woods or by reducing the effect of light by incorporating ultra-violet absorbers therein. It has now surprisingly been found that it is possible to achieve a more satisfactory result than in the past by a particular oxidation of ligneous ingredients. By means of the invention a stabilised colour may be imparted to the material, so that for example only slight or imperceptible changes take place in that colour even after quite long exposure to light. The invention is particularly applicable to solid wood or wood in the form of a veneer. It has also been found that by a similar method a stabilised colour may be given to other ligno-cellulosic materials (such as jute, ramie, sisal and flax).

The invention provides a method for producing stable colour in ligno-cellulosic material which comprises treating the material with an oxidising agent so as to oxidise natural substances present in the material whereby there are produced oxidation products which are substantially stable to light, so that the colour of the material containing such oxidation products is stabilised.

The oxidising agent may of course be a mixture of oxidising agents. As indicated above, the oxidising agent produces relatively light-stable oxidation products in the material. Persulphates and hypochlorites (for example ammonium or alkali metal persulphate or hypochlorite) either separately or in combination with other agents such as peroxides have been found particularly satisfactory in producing a good stable colour. Hypochlorous acid (for example with pH of 2 to 7) is in some cases very suitable, or the oxidising agent may be obtained by adding free acid to an alkaline solution of hypochlorite. If a hypochlorite is used, it may be an alkaline solution containing at least 0.1% of available chlorine. If a persulphate is used, it may be a solution containing from 10 g. up to the solubility limit thereof. Chlorates and perchlorates have been found somewhat less suitable because the colour produced is less stable; nitrates may give an inadequately stable colour for some purposes. Other contemplated oxidising agents include iodates, periodates,

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bromates and perbromates, but these are rather expensive.

The oxidising agent is normally applied to the material, but it may sometimes be found convenient to produce it in situ in the material, for example by applying to the material substances which will react to form the oxidising agent.

The oxidising agent may be applied to the material in the form of a solution thereof. The material is preferably completely immersed in the solution, or treated therewith by swabbing or the like.

The oxidation must, of course, be a fairly gentle one so as not to destroy the nature of the material, but it may be sufficiently strong so that the oxidation products have a colour somewhat different from the colour of the material before treatment.

This confers a further advantage on the invention in that it can be used for the additional purpose of providing the treated material with a greater uniformity of colour than it had before treatment. By this means different samples of material (particularly wood) within the same species may be given more similar colours and this facilitates matching of materials of the same species from different sources.

This advantage is of particular value in the furniture industry. A furniture factory frequently has to get its supplies of wood of one species from a number of different sources. It would often happen that pieces of wood from different sources would be brought together in a single piece of furniture, but hitherto this has often had to be avoided because the different pieces of wood, although of the same species, have often had different colours, so that a piece of furniture containing them would be commercially unacceptable. By means of the present invention, this source of inefficiency in furniture manufacture can be avoided, as the wood from the various sources can be treated by the present method so as to be more uniform in colour.

A further advantage is that the method of the invention can be used to confer greater uniformity of colour in a single piece of wood. Thus, it sometimes occurs that exposure of part of the surface of a piece of wood to light causes localised discolouration or darkening, leaving a patchy appearance. Treatment of the surface by the present method can bring the variously coloured portions into greater colour uniformity.

In using the method of the invention, one will naturally select in each particular case an oxidising agent or agents which will not give the wood an undesirable colour, or give rise to other undesirable side effects. Thus, one will usually avoid the use of large proportions of potassium permanganate.

It is, of course, not necessary to treat the full thickness of a piece of the material of which only the surface is to be seen in use. It has been found generally adequate in practice to treat the wood to a depth of up to 1 mm. and a stabilised layer of this thickness is frequently more than adequate.

It is frequently found desirable to use an oxidation catalyst (for example one containing permanganate or cupric ions) so as to accelerate the oxidation, and thus save time in carrying out the process. The oxidation catalyst may for example be applied as a single solution with the oxidising agent, or as a separate solution.

The most suitable oxidising agent, solvent, pH concentration, time of application and the like may vary from wood to wood and may partly depend on the particular final colour and the thickness of the stabilised layer which is desired. The most suitable parameters can in any particular case be found by tests involving variation of the parameters indicated above.

An important preferred feature of the invention is the control of the pH during the oxidation. It has been found that the colour and its stability may partly depend on the pH. Frequently it is very desirable to apply pH adjusting agents to the material so as to impart a suitable pH during treatment; generally an alkaline pH is advantageous, but in particular cases (especially teak) an acid pH may be desirable.

The pH adjusting agent may for example be as a single solution with the oxidising agent, or as a separate solution. Many oxidising agents (such as persulphates) have been found to form acid reaction products when applied in the present process; if it is found that these acid products, particularly if added to the natural acidity of many woods, cause too low a pH, then a suitable alkaline agent may be applied to the material. Sometimes the required pH may be maintained by means of a pH buffer, for example a phosphate or acetate buffer.

It is generally convenient to use the oxidising agent in the form of a solution containing a pH adjusting agent to impart a predetermined pH (optionally with at least 0.1 g. of an oxidation catalyst per litre) the remainder of the solution consisting essentially of water with or without a lower alcohol and optionally containing a surface-active agent.

Where the treatment imparts an acid or alkaline pH to the material, it may be desirable to bring the pH to a moderate value, say 5-8, by treatment of the material with an alkaline or acid material.

The single oxidising step may leave a surface layer of wood which is not only stabilised in colour but which has an acceptable colour. This has been found to be the case with, for example, African mahogany and European walnut.

In many cases, it has been found desirable to effect the method in stages, the first stage being as described above and the second stage being a second treatment with a second oxidising agent so as to modify the stabilised colour (which may reinforce stabilisation); this has been found desirable in, for example, the cases of afrormosia, African walnut, teak and gaboon. Hypochlorite and hydrogen peroxide are examples of second oxidising agents which have been found beneficial in certain cases. For example, medium dark stabilised shades of colour have successfully been produced in African walnut and in afrormosia by using a persulphate as first oxidising agent and a hypochlorite as a second oxidising agent. A golden yellow stabilised colour has been obtained in teak by the use of a persulphate as first oxidising agent and hydrogen peroxide as second oxidising agent. A pale stabilised colour has been obtained in sycamore and in gaboon by the use of a hypochlorite as first oxidising agent and hydrogen peroxide as a second oxidising agent.

When the oxidising agent is a hypochlorite, it is sometimes advantageous to precede the treatment with hypochlorite by a pre-treatment with a persulphate; this is particularly the case with many light-coloured woods, such as European beech, Douglas fir and oak. This pre-treatment has been found to intensify the effect of the hypochlorite as main oxidising agent. After the treatment with hypochlorite, a further treatment with a second oxidising agent, particularly hydrogen peroxide, may be employed as mentioned in the last paragraph above.

A final stage of washing the material with a liquid of pH other than 7 is a desirable optional feature of the method of the invention for the purpose of neutralising any excess acidity or alkalinity of the surface of the material and giving it a pH of 5-8. This liquid can also act as a wash to remove any unwanted solid substance on the surface of the material.

After treatment by the method of the invention, the material may be dried in air or force-dried, for example by a current of heated air. Some time is desirably allowed to elapse between the treatment and the force-

drying; the minimum time varies from wood to wood, but a time of at least 5 minutes is generally required for best results.

In addition to the above general teaching, the invention provides specific guidance to cover most practical cases. In particular, the following ranges of compositions are an important feature of the invention.

For the first stage of the method of the invention, it is preferred to use as oxidising agent, particularly for dark or medium coloured woods such as sapele (*Entandrophragma cylindricum*), African mahogany (*Khaya ivorensis*), afrormosia (*Afrormosia elata*), muninga (*Pterocarpus angolensis*), utile (*Entandrophragma utile*), iroko (*Chlorophora excelsa*), tola (*Oxy stigma oxyphyllum*), African walnut (*Lovoa klaineana*), teak (*Tectona grandis*) and European walnut (*Juglans regia*), a solution containing from 10 g. per litre up to the solubility limit of potassium, sodium or ammonium persulphate, the remainder of the solution consisting essentially of water and a lower alcohol and optionally a surface-active agent (such as 5-15 ml. of teepol or lissapol). Such a solution is herein called "solution A."

For light-coloured woods (such as oak, beech, birch, sycamore, gaboon (*Aucoumea klaineana*), Douglas fir, ash or maple) it has been found advantageous to use as first oxidising agent an alkaline hypochlorite solution containing 1-5% of available chlorine. Such a solution is herein called "solution A1."

For the second oxidising stage (if one is used), it is preferred either to use a solution containing, per litre, sodium hypochlorite in an amount equivalent to 100-500 ml. of a sodium hypochlorite solution of 10-12% available chlorine, and a pH adjusting agent in an amount to give the desired pH, the remainder consisting essentially of water, or to use a 10-100 volumes hydrogen peroxide solution which desirably contains 1-5% ammonium acetate by weight. Such a solution is herein called "solution B." The sodium hypochlorite solution is generally used when a persulphate has been used as the first or main oxidising agent (that is, in many cases where solution A has been used). The hydrogen peroxide solution is generally used after solution A in the case of teak, and after solution B in the case of light-coloured woods.

In its application to the material, the selected solution is in each case preferably swabbed on to the surface of the material for approximately 5 minutes. Between successive stages a period of time is preferably allowed for drying; this time may be reduced by force-drying, for example in a current of warm air. Desirably the material is allowed to remain at least five minutes at room temperature.

If the material to be treated is sapele, African mahogany, afrormosia, muninga, utile, iroko or tola, and the final colour is to be light, then it may be treated in a first stage with a solution A (having an alkaline pH), in a second stage with a solution B (having an alkaline pH) and in a final stage with a solution of a weak acid (for example containing 20-100 ml. of glacial acetic acid per litre) to restore the pH to 5-8. In this case preferred solutions A and B contain respectively the following ingredients in approximately the following amounts per litre: (A) 30 g. of potassium persulphate, 30 g. of sodium carbonate, 0.5 g. of potassium permanganate, 150 ml. of methylated spirit, 10 ml. of teepol or lissapol, and water to make up a litre; (B) 200 ml. of sodium hypochlorite solution containing 10-12% available chlorine, 10 g. of sodium carbonate, and water to make up a litre.

If the material to be treated is European walnut, or if it is sapele, African mahogany or utile, and the final colour is to be dark, then it may be treated in a first stage with a solution A (having an alkaline pH) and in a second, final stage with a solution of a weak acid (for example containing 20-100 ml. of glacial acetic acid

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per litre) to restore the pH to 6-8. In this case a preferred solution A contains the following ingredients in approximately the following amounts per litre: 30 g. of ammonium persulphate, 100 ml. of 0.88 ammonia, 0.5 g. of potassium permanganate, 150 ml. of methylated spirit, 10 ml. of teepol or lissapol, and water to make up a litre.

If the material to be treated is African walnut or if it is afrormosia and the final colour is to be medium dark, then it may be treated in a first stage with a solution A (having an alkaline pH), in a second stage with a solution B (having an alkaline pH) and in a third stage with a solution of a weak acid (for example containing 20-100 ml. of glacial acetic acid per litre) to restore the pH to 6-8. In this case preferred solutions A and B contain respectively the following ingredients in approximately the following amounts per litre: (A) 30 g. of ammonium persulphate, 100 ml. of 0.88 ammonia, 0.5 g. of potassium permanganate, 150 ml. of methylated spirit, 10 ml. of teepol or lissapol, and water to make up a litre; (B) 200 ml. of sodium hypochlorite solution containing 10-12% available chlorine, 10 g. of sodium carbonate and water to make up a litre.

If the material to be treated is teak and the final colour is to be golden yellow, then it may be treated in a first stage with a solution A (having an acid pH) and in a second, final stage with a solution B. In this case preferred solutions A and B contain respectively the following ingredients in approximately the following amounts per litre: (A) 60 g. of ammonium persulphate, 30 ml. of concentrated hydrochloric acid, 0.5 g. of cupric sulphate, 150 ml. of methylated spirit, 10 ml. of teepol or lissapol, and water to make up a litre; (B) 50 volumes hydrogen peroxide containing 2% of ammonium acetate by weight.

It has been found that, in general, pink or light red woods may be treated with the same solutions as sapele and African mahogany, while beige or pale brown woods may be treated with the same solutions as utile, iroko and tola.

After treatment by the method of the invention, the material may be subjected to a conventional finishing operation. For example, wood may be finished by de-nibbing or sanding after filling or sealing. Heavy sanding is desirably avoided as it may remove the layer stabilised by the method of the invention, if such layer (as is usual) is not more than one millimetre thick.

When using the method of the invention to bring differently coloured samples of the same species of wood into greater colour uniformity, it may be advantageous to apply to the lighter coloured samples a solution which has a darkening effect as well as a stabilising effect, and to the darker samples a solution which has a lightening effect on colour as well as a stabilising effect. A solution B frequently has a lightening effect and a solution A a darkening effect. These solutions are suitably used at half the strengths indicated herein, and may be followed by the treatment with acetic acid solution, the latter being used at full strength. For example, in order to bring different samples of afrormosia into greater colour uniformity, the darker samples may be treated with a half-strength solution B and the lighter samples with a half-strength solution A, followed in both cases by treatment with acetic acid solution of the strength hereinbefore indicated.

The invention also provides ligno-cellulosic materials (especially solid woods and veneers) treated by the method of the invention, as well as furniture and other artifacts made of or containing such treated material.

It is important to note that the process of the invention not only produces stabilised colours; it also enables different colours to be obtained by variation of the parameters mentioned above, such as the pH, the nature and strength of the oxidising agent, and the use of more than one treatment with different agents.

The invention is illustrated by the following examples.

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EXAMPLE 1

Sapele

A solution A was used containing 50 g. of potassium persulphate, 50 g. of sodium carbonate, 0.5 g. of potassium permanganate, 150 ml. of methylated spirit, 10 ml. of teepol and enough water to make up one litre. The solution was applied to a sample of sapele by swabbing for about 2 minutes. The sapele was then allowed to dry for about an hour. It was then swabbed for about 2 minutes with a solution B containing 200 ml. of a sodium hypochlorite solution containing 10-12% of available chlorine, 10 g. of sodium carbonate and water to make up a litre. The sapele was then allowed to dry for an hour. It was then swabbed for about 2 minutes with a solution of acetic acid containing 50 ml. of glacial acetic acid and water to make up a litre. It was then completely dried and coated with one layer of a clear nitrocellulose lacquer.

The treated sapele panel and a control (untreated) panel were exposed to a north light for eight weeks, their reflectance being measured before and after such exposure. The results are given in Table 1. The treated panel had a much more stable colour than the control panel.

EXAMPLE 2

African walnut

A panel of African walnut was treated as described in Example 1 except that solution A contained 50 g. of ammonium persulphate and 100 ml. of 0.88 ammonia instead of the potassium persulphate and sodium carbonate.

The reflectance results obtained with the treated panel and a control panel are given in Table 1. The treated panel had much more stable colour than the control panel.

EXAMPLE 3

Afrormosia

A panel of afrormosia was treated as described in Example 1.

The reflectance results obtained with the treated panel and a control panel are given in Table 1. The treated panel had a much more stable colour than the control panel.

EXAMPLE 4

Teak

A panel of teak was swabbed for about 2 minutes with a solution A containing 60 g. of ammonium persulphate, 30 ml. of concentrated hydrochloric acid, 0.5 g. of cupric sulphate, 150 ml. of methylated spirit, 10 ml. of teepol and water to make up a litre. After being allowed to dry for about half an hour, the panel was swabbed for about 2 minutes with hydrogen peroxide solution of 50 volumes strength, containing 2% of ammonium acetate. The panel was coated with one layer of clear nitrocellulose lacquer after final drying.

The treated panel was found to have a much more stable and better colour than an untreated control.

EXAMPLE 5

European oak

A panel of European oak (*Quercus robur*) was pre-treated being immersed for about 5 minutes in a solution containing 30 g. of potassium persulphate, 30 g. of sodium carbonate, 0.5 g. of potassium permanganate, 150 ml. of methylated spirit, 10 ml. of surface-active agent and water to make up a litre. It was allowed to dry. It was then immersed for about 5 minutes in a solution A1 of sodium hypochlorite containing 3% of available chlorine and 2% of sodium carbonate. It was then dipped, while still wet, into a solution of hydrogen peroxide of 40 volumes strength, with agitation. The wood was finally rinsed with water and dried.

The panel then retained a stabilised light colour for eight months in normal daylight, while a control (un-

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treated) panel of the same wood assumed a deep yellow colour.

The reflectance results obtained before and after the first 8 weeks of the exposure to daylight are given in Table 2.

EXAMPLE 6

Jute

A sample of jute was immersed for about 5 minutes in a solution A similar to that of Example 1 except that it contained 30 instead of 50 g. of the persulfate and of the sodium carbonate per litre. The jute was dried. It was immersed for about 5 minutes in a solution of acetic acid containing 50 ml. of glacial acetic acid and water to make up a litre.

The treated sample was found to be much more stable in colour than a control (untreated) sample.

TABLE 1

Reflectance values obtained with the FIRA Spectrophotometer, using nine Ilford colour filters Nos. 601-609. Readings were taken of test panels and controls before and after an eight-week period of exposure to the north light. The values in the table represent percent reflectance of a Chrome Yellow surface, used as standard (reflectance=100%).

The values for controls are given in parentheses.

B=before exposure
A=after exposure
T=treated specimens
C=control

		Filter Nos.																		
		601		602		603		604		605		606		607		608		609		
		Peak transmission, mμ																		
		425		470		490		520		550		580		600		660		685		
		Wood																		
		T	C	T	C	T	C	T	C	T	C	T	C	T	C	T	C	T	C	
<i>Entandrophragma cylindricum</i>		{B---	79	(81)	74	(79)	46	(50)	46	(48)	48	(50)	42	(45)	48	(53)	65	(72)	73	(80)
(Sapele):		{A---	74	(71)	74	(69)	46	(42)	46	(43)	45	(42)	43	(39)	48	(44)	64	(58)	74	(67)
<i>Louoa klaineana</i> (African walnut):		{B---	71	(76)	69	(74)	43	(51)	43	(49)	42	(51)	39	(50)	43	(57)	57	(71)	66	(80)
		{A---	71	(74)	70	(72)	45	(46)	44	(46)	44	(45)	40	(42)	44	(47)	59	(60)	67	(69)
<i>Afrormosia elata</i> (Afrormosia):		{B---	73	(76)	72	(74)	46	(50)	48	(50)	46	(49)	43	(48)	48	(53)	64	(67)	72	(77)
		{A---	73	(74)	72	(72)	46	(45)	46	(45)	46	(44)	43	(41)	48	(45)	64	(58)	72	(66)

Visual assessment of the treated specimens eight months after the treatment did not indicate further changes in colour of treated samples of sapele and afrormosia: very slight fading had occurred in African walnut.

TABLE 2
[Reflectance changes for white oak]

	Filters								
	1	2	3	4	5	6	7	8	9
Before exposure.....	76 (97)	77 (97)	59 (72)	54 (63)	55 (66)	59 (67)	66 (71)	80 (86)	93 (96)
After exposure.....	79 (87)	79 (87)	60 (64)	55 (61)	57 (60)	60 (61)	68 (66)	82 (80)	93 (90)

What I claim is:

1. A process for producing stable colour in a wood comprising subjecting wood selected from the group consisting of sapele, African mahogany, African walnut, afrormosia, muninga, utile, iroko and tola to a first treatment with a persulfate oxidising agent under alkaline conditions, subjecting the wood to a second treatment with a hypochlorite oxidising agent under alkaline conditions and then adjusting the pH to from about 5 to about 8 with a weak acid whereby a stabilised colour is imparted to the wood.

2. A process according to claim 1 wherein the persulfate is selected from the group consisting of potassium and ammonium persulfate.

3. A process according to claim 1 wherein the pH adjustment is effected with acetic acid.

4. A process according to claim 1 wherein the persulfate oxidising agent is catalysed with a catalyst selected from the group consisting of permanganate and cupric ions.

5. A process according to claim 1 wherein the wood being treated is sapele.

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6. A process according to claim 1 wherein the wood being treated is African mahogany.

7. A process according to claim 1 wherein the wood being treated is African walnut.

8. A process according to claim 1 wherein the wood being treated is afrormosia.

9. A process according to claim 1 wherein the wood being treated is muninga.

10. A process according to claim 1 wherein the wood being treated is utile.

11. A process according to claim 1 wherein the wood being treated is iroko.

12. A process according to claim 1 wherein the wood being treated is tola.

13. A process according to claim 1 wherein an aqueous potassium persulfate solution is employed containing per liter about 30 gm. of potassium sulfate, about 30 gm. of sodium carbonate, about 0.5 gm. of potassium permanganate, about 150 ml. of methylated spirit, about 10 ml. of teepol or lissapol, and water to make up a liter, and the hypochlorite is added as an aqueous solution containing per liter about 200 ml. of sodium hypochlorite solution containing about 10-12% available chlorine, and about 10 gm. of sodium carbonate.

14. A process according to claim 1 wherein the pH adjustment is effected with an aqueous solution that contains from about 20 to about 100 ml. of glacial acetic acid per liter of solution.

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