United States Patent [19]

Hill

[11] **3,850,683**

[45] **Nov. 26, 1974**

[54] **IRON STAIN INHIBITORS**

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[22] Filed: **June 12, 1973**

[21] Appl. No.: **369,222**

[52] **U.S. Cl.**..... **117/147,** 106/286, 106/287 R, 117/151

[51] **Int. Cl.**..... **B27k 3/18,** B27k 5/00

[58] **Field of Search**..... 106/2, 286, 287 R; 117/147, 151, 57

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[57] **ABSTRACT**

Wood is treated in inhibit the iron staining of the wood during shipment in commerce by applying to the wood prior to shipment finely divided insoluble salt of a Group II Metal (beryllium, magnesium, calcium, strontium, barium,, zinc, cadmium and mercury). The preferred anti-stain compounds are the insoluble salts of calcium, zinc and magnesium, particularly zinc oxide and calcium carbonate.

16 Claims, No Drawings

IRON STAIN INHIBITORS

BACKGROUND OF THE INVENTION

This invention is directed to a treatment for wood to protect the same from iron staining during shipment, especially when shipment is by railway. More particularly this invention is directed to the protection of wood from in-transit iron staining comprising treating the wood with an insoluble salt of a Group II Metal.

It is well known that when lumber or other wood products are shipped uncovered on open railway cars, they usually arrive with considerable discoloration of the exposed surfaces. This discoloration occurs to both green and dry wood. The principal cause of this discoloration is the iron staining of the wood. The iron which causes the staining problem arises from (1) wear on the brakeshoe linings, (2) wear of the wheels on the rails, and (3) iron particles derived from steel mill slag which is used by many railroads as part of the ballast on the railroad beds for stability, drainage, etc. The iron particles are blown onto the surfaces of the transported lumber shipments along with dust and dirt. The staining action is activated by atmospheric precipitation such as heavy dew, rain, sleet, snow, etc. Iron staining of susceptible lumber other than during rail transit may be encountered in areas of heavy contanimation and at sites adjacent to railway tracks. The problem of iron staining is reported rarely encountered in lumber shipped by boat.

It is believed that the ground up and abraded iron particles reach the lumber loaded on the open rail cars by one or more of the following means: (1) through air currents and/or partial vacuum created by movement of the train; and/or (2) through an electrostatic field which is apparently created around the moving train and which apparently consists largely of negatively charged dust particles. Such an electrostatic field apparently attracts and keeps in suspension the finely divided positively charged iron particles thus affording them ample opportunity to come in contact with all exposed surfaces of the wood.

After the iron dust settles on the wood surfaces, it is activated in the presence of moisture and oxygen and the staining action discolors the wood. Because the lumber is generally strapped in bundles only the external exposed surfaces are usually stained.

Because sufficient iron, oxygen, and moisture are normally present, all wood shipped on railway cars is usually very severly stained when it reaches its destination. Heretofore, the most common method for preventing iron staining was to wrap the lumber in paper or plastic or ship the lumber in closed boxcars. However, both of these methods are expensive and time consuming. In addition, lumber wrapped in paper or plastic has a tendency to tear under the normal conditions of rail transit. Disposal of the paper and plastic creates an additional problem.

More recently it has been suggested to treat the wood prior to shipment with an anionic antistatic agent or a chemical chelating agent for iron or a combination of the antistatic agent and the chelating agent. See Kelso et al., U.S. Pat. No. 3,630,763. However, these treatments are expensive and are not as effective as desired. It has also been suggested that the iron stain may be removed from the lumber with a chemical bleaching compound. Examples of some of the chemical bleaching compounds are oxalic acid, orthophosphoric acid, hydrogen peroxide, sodium bisulfite, and sodium hypochlorite. See for example Story, U.S. Pat. No. 3,473,947. However, these treatments are also expensive and not as effective as desired.

It is therefore, the object of this invention to provide an improved method for preventing the in-transit iron staining of green and dry wood.

SUMMARY OF THE INVENTION

I have discovered an improved method for preventing the in-transit iron staining of green and dry wood. The method of my invention is inexpensive and more reliable than the prior art methods. Lumber treated according to my invention arrives at its destination in essentially mill bright condition without having to be wrapped in paper or shipped in a closed boxcar.

The method of my invention comprises treating the wood prior to shipment with finely divided insoluble salts of the Group II Metals. The useful Group II Metals are beryllium, magnesium, calcium, strontium, barium, zinc, cadmium, and mercury. The preferred Group II Metals are calcium, zinc, and magnesium. The finely divided insoluble salts will generally have an anion portion selected from the group of oxide, hydroxide, carbonate, borate, silicate, chromate, and phosphate.

The metal salt is applied to the wood as a dispersion of finely divided particles in a suitable liquid vehicle. The dispersion may be applied by brushing, dipping, spraying or any other convenient technique.

As mentioned above, the metal salts are applied as dispersions (emulsions, suspensions, etc.) of finely divided particles in a suitable vehicle. The dispersions should contain a minimum of 0.1 percent by weight of the metal salt. If dispersions containing less than this amount are used, no appreciable stain prevention is obtained. The upper concentration of metal salts in the dispersion is not critical and is largely determined by an economic consideration. Generally the upper limit will seldom exceed 20 percent by weight. Above concentrations of about 10 percent no increase in effectiveness of iron stain inhibition would be obtained for a corresponding increase in concentration. In addition, dispersions containing greater than about 20 percent by weight of the finely divided metal salts may be in certain dispersions systems too viscous to apply and also some systems at 20 percent concentration form a white coating which easily rubs off without a suitable binding vehicle. The preferred concentration of metal salts in the dispension is from about 1 percent to about 10 percent. It should also be noted that the minimum effective concentration of antistain compounds is also dependent to a certain extent on the particular wood being treated and the method used for application. The most effective concentration for a particular wood and particular method of application can be determined by routine experimentation.

The finely divided metal salts may be dispersed in any suitable liquid medium. The most convenient and readily available medium is water. Aqueous dispersions of the Group II Metal salts are easily prepared and applied to the wood. However, the finely divided metal salts may readily be dispersed in an organic medium such as an alcohol, paraffin oil, mineral spirits and the like. It is also within the scope of this invention to use a liquid medium which is a combination of water and an organic liquid. This is particularly true for the min-

eral spirits which are commonly employed along with water in standard paint formulations.

In addition to the finely divided metal salts, the dispersions may also contain other additives. For example, it is most beneficial to apply a water repellent compound to the wood at the same time. The use of a water repellent with the anti-stain compounds of the present invention increases the effectiveness of the anti-stain compounds. However, the use of the water repellent alone is insufficient to inhibit iron staining. Therefore, the finely divided metal salts may be dispersed in a formulation containing a water repellent. In addition, other wood preserving and wood treating compounds may be used in the formulation.

The use of dispersing agents are not essential to the prevention of iron staining so long as the anti-stain materials are finely ground and kept suspended until application. However, the use of a dispersing agent is desirable. The effect of a satisfactory dispersing agent is to more finely break up the agglomerates of the finely divided powdered Group II Metal salts. This results in a smaller particle size distribution and also lowers the viscosity of the high or concentrated dispersions. This is important in emulsifiable concentrates containing water repellents in addition to high percentages of the anti-stain agents. This is particularly true for products formulated for further dilution with water. In many cases, the concentrate is a semi solid in the absence of dispersing agents for the anti-stain compounds. The presence of the dispersing agents also affect the appearance of the treated wood. For example, the use of a finely divided zinc oxide even at a 4–5 percent level in a ready to use formulation is barely discernable on the treated wood when a suitable dispersing agent is employed. However, in the absence of the dispersing agents, the larger size distribution of the zinc oxide leaves a white colored treatment after drying.

The dispersions of anti-stain compounds may be applied to the lumber by spraying, brushing, dipping or any other convenient method. The easiest method is to spray the exposed surfaces of the lumber which is loaded on the transit vehicle. The minimum coverage is about 1 gallon per thousand square feet of exposed lumber. For example, Western Hemlock and Douglas fir kiln dried lumber on a quick dip or immersion application will take up about four gallons of an aqueous emulsion per thousand square feet of surface area. A coverage of 2–3 gallons per thousand square feet is a good average when using an aqueous spray application to southern pine.

The application rate must be high enough to wet the wood continuously and not leave areas of untreated surface. It is more desirable to adjust the concentration of suspended anti-stain agents so that the application rate gives thorough coverage. An application rate of from about 1 gallon to about 6 gallons per thousand square feet of exposed surface is the practical range. An overtreatment will just run off the boards in most cases and is not recoverable. The application to different species at different moisture contents will fall within the practical range since commercial applications would be very rapid. It is extremely doubtful that one would use production times for long periods of soaking the lumber.

As mentioned supra, the anti-stain compounds of the invention are the insoluble salts of the Group II Metals. The useful Group II Metals have been defined as beryllium, magnesium, calcium, strontium, barium, zinc, cadmium, and mercury. The preferred metals are magnesium, calcium, and zinc. By insoluble is meant those salts having a solubility of less than about 0.5 percent by weight in water at room temperature and at an essentially neutral pH. If the Group II Metal salts are soluble in water, they will be leached from the wood and hence be ineffective.

The Group II Metal salts may have any anion. However, the most common and useful finely divided compounds are the oxides, hydroxides, carbonates, bornates, silicates, chromates, and phosphates of the useful Group II Metals. As is realized by one of ordinary skill in the art, some of the salts are colored and will therefore impart a color to the treated wood. The preferred anti-stain agents which do not impart a color other than white to the wood are zinc oxide, calcium carbonate, and tricalium phosphate. The zinc oxide is the most preferred compound since it has fungistatic activity and hence an added benefit for protection of microorganism growth of the sapwood of the treated species. The zinc chromates are preferred if a yellow color is desired. The chromates and other colored anti-stain agents may be used in combination with calcium carbonate, zinc oxide or other non-coloring anti-stain agents to give anti-stain agents with various intermediate colors. Non reactive colored pigments may also be used to impart desired colors to the anti-stain agents. It may also be desirable to mix one or more of the various finely divided Group II Metals for economic reasons. Therefore, it is within the scope of this invention to use as the anti-stain agent a combination of two or more different finely divided insoluble Group II Metal salts.

As stated above, the insoluble Group II Metal salts are finely divided. It is necessary that the anti-stain compounds are finely divided in order that they may be readily dispersed and applied to the wood. If the metal salts are not finely divided, they will not adequately protect the wood when sprayed or brushed on. In addition, if the metal salts are not finely divided, a large excess is necessary in order to be effective. Therefore, the metal salts should be finely divided, that is of pigment grade. Perferably, the finely divided metal salts should have a particle size of less than about 1 micron.

The anti-stain compounds of this invention are effective against all the various types of wood which are susceptible to iron staining. Examples of some of the various woods are the softwood species such as Douglas fir, white spruce, white fir, lodgepole pine, hemlock, Alaskan Yellow cedar, ponderosa pine, sugar pine, and southern pine. Examples of some of the hardwood species are red oak, white oak, cottonwood, pecan, and hickory. The wood may be green or kiln dried. In addition, the wood may be lumber, plywood, fiberboard, particle board and the like.

Numerous experiments have been performed demonstrating the effectiveness of these inventions. The following are examples of some of these experiments. These examples should be construed to illustrate the invention but not to limit the same.

EXAMPLE 1

A series of dispersions of zinc oxide were prepared to determine the minimum concentration of the anti-stain compounds which would be effective. A pigment grade zinc oxide was sheared into water to form a dispersion

concentrate. No dispersing agents were employed and the dispersions were prepared with a Waring Blender. Dilutions of the concentrate were made so the resulting dispersions contained 0.1, 0.25, 0.50, 1.0, 2.0, and 3.0 percent by weight of the zinc oxide in water. The dilutions were kept agitated to prevent settling and applied to freshly planed, kiln dried, Douglas fir, western red cedar, and western hemlock boards with a paint brush. Any excess dispersion was allowed to drain off by tilting the surface to a verticle position.

After drying, pieces of finely divided steel wool fibers were sprinkled onto the treated and untreated areas. Then from one to two milliliters of water were dropped on the steel wool covered surfaces. The water spots were kept wet for two hours with addition of more distilled water after which the boards were allowed to dry overnight. The iron stain inhibition was determined by comparing the treated with the untreated wood. On Douglas fir and western red cedar, the stains were a very dark blue color and on hemlock the stains were a greenish gray.

The results for Douglas fir showed that on the surface treated with 0.1 percent zinc oxide, there was little or no change when compared to the control. However, at 0.25 percent zinc oxide concentration, there was 70 percent less staining than the control. The higher concentrations of zinc oxide gave essentially 100 percent iron stain inhibition. The western red cedar had no stain inhibition at the 0.1 percent and 0.25 percent zinc oxide levels. At the 0.5 percent zinc oxide there was a 50 percent inhibition and the higher concentrations completely inhibited the iron staining. The western hemlock showed a 30 percent inhibition at the 0.1 percent zinc oxide level and complete inhibition at the higher levels (1.0 percent and above).

The above results illustrate that the effective minimum concentration is somewhat dependent on the type of wood being treated. However, a concentration of 0.1 percent appears to be the minimum effective amount.

EXAMPLE 2

A series of dispersions of various finely divided Group II Metal salts in a non-aqueous medium were prepared and evaluated. The iron stain inhibitors were dispersed in oil borne systems. The formulation as applied to fir was as follows: Federal Specification TTW-572-B wood preservative containing 5 percent pentachlorophenol with a low resin and wax content (96 percent by weight) and finely divided iron stain inhibitors (4 percent by weight). The Group II Metals that were used were zinc oxide and zinc chromate. These compounds were sheared into the mineral spirits solution without any added dispersing aids. The insoluble finely divided inhibitors were kept suspended by agitation until applied to the wood. They were applied to wood samples which were then nailed to the top of rail carloads for transcontinental shipment. After transcontinental shipment, the wood samples were evaluated. The results illustrated that the anti-stain compositions controlled in-transit iron staining. This system imparts both anti-stain and water repellency to the lumber. The method of application was a dip treatment.

EXAMPLE 3

The following are examples of some formulations which contain the antistain agents alone and in combination with a water repellent. A specific formulation developed which contains a combination of anti-stain agents in a water repellent emulsion concentrate is as follows:

Ingredient	Percent by Weight
Rohm and Haas, Ta-mol SN (sodium salt of a condensed arylsulfonic acid)	0.4
Sodium Gluconate	2.0
ABEX 18S (surfactant)	2.0
Water	30.6
Calcium Carbonate	5.0
Zinc Oxide	15.0
Mineral Spirits	30.0
126/130 F.M.P. Paraffin Wax	1.5
Pentaerythritol ester of a mixture of 75% Rosin acids and 25% Tall Oil Fatts acids	13.5

An aqueous dispersion was prepared by dissolving the Tamol SN and Sodium gluconate in the water in a Waring Blender and at a high rate of shear. Then the zinc oxide and calcium carbonate were added with continued shearing for about five to ten minutes. An oil phase was prepared which was a solution of the pentaerythritol ester and paraffin wax in the mineral spirits. The finished concentrate was prepared by adding the oil phase slowly to the aqueous phase at a high rate of shear in the Waring Blender. The resulting viscous but pourable concentrate was found to be stable after storage in a sealed glass bottle for greater than three weeks at 120° F.

During storage the anti-stain agents did not measurably react with the water repellent system nor did the mixture form a hard cake in the bottom of the concentrate. The concentrate was stable to freeze thaw cycles. When the concentrate was diluted with four volumes of water a stable white emulsion was formed. The anti-stain agents settled out slowly to form a soft redispersible cake but a stable system could be maintained with mild agitation. When the dilution was applied to western hemlock, western red cedar and Douglas fir, the emulsion wetted the wood evenly and upon drying, left a barely perceptible but light colored treatment which had penetrated into the outer surface of the wood and would ball up and hold out water droplets. The treated wood exhibited excellent stain control using the wet steel wool tests.

This formulation may be varied by using all zinc oxide or all calcium carbonate at the 20 percent anti-stain level. In addition, other anti-stain agents may be substituted for the zinc oxide or calcium carbonate. Other dispersants may also be employed. For example, it has been found that sodium lignosulfonate at concentrations of 5–10 percent by weight based on the weight of the dry anti-stain agent is very effective.

Another specific formulation developed is as follows:

	Percent by Weight
Paracol 404A or 404N	50
Sodium lignosulfonate	2
Calcium Carbonate	15
Zinc Oxide	5
Water	28

This concentrate is of low viscosity and represents a very economical concentrate for dilution with water.

Both of the above concentrates when diluted properly do not leave a coating on the wood as would a film forming paint. It should be noted that the concentrated formulations are similar to standard paint formulations.

EXAMPLE 4

A series of Douglas fir boards were prepared for in-transit testing. The boards were treated in one of the following manners:

1. A mineral spirits or stoddard solvent solution containing water repellents and 5 percent pentachlorophenol meeting Federal Specification TT-W-572B was prepared. The finely divided oil and water insoluble anti-stain compounds were dispersed in the solution and were applied as a single dip treatment.

2. An aqueous dispersion of the finely divided anti-stain compounds was applied to the wood by a single dip treatment.

3. A two step treatment in which the anti-stain chemical was applied by dipping in the aqueous dispersion of (2) above followed by a dip treatment of a water repellent. The water repellent was 90.8 percent mineral spirits, 7.2 percent pentaerythritol ester, and 2.0 percent 126/130 melt point paraffin wax.

The test specimens were kiln dried Douglas fir heartwood which were 2 × 4 inch specimens. The treatments were applied by dipping for 15 to 20 seconds. Duplicate sets of the specimens were treated and sent from Washington State to Newark, New Jersey by rail, nailed to the top of lumber shipments. Evaluation of the specimens after transcontinental shipment gave the following results:

Anti-Stain Compound	Treatment	% Inhibition
8% $CaCO_3$	(1)	90%
4% ZnO	(3)	do.
4% ZnCrO & 0.4 Harshaw Red Oxide	(2)	do.
4% $ZnCrO_3$ & 0.4 Harshaw Red Oxide	(3)	do.
4% $CaCO_3$	2	do.
4% $CaCO_3$	3	do.
4% ZnO	1	do.
1% $ZnCrO_3$ & 3% $CaCO_3$	3	do.
4% $ZnCrO_3$	3	do.
2% $CaCO_3$ & 2% $ZnCrO_3$	3	do.
4% ZnCrO	1	do.
4% $CaCO_3$	1	do.
4% basic $ZnCrO_3$	1	do.
None	3	None
None	1	None
None	None	None
4% EDTA	3	None

What is claimed is:

1. A method for treating wood to prevent the iron staining of the wood comprising applying to the wood a dispersion of a finely divided insoluble Group II Metal salt selected from group consisting of beryllium, magnesium, calcium, strontium, barium, zinc, cadmium and mercury.

2. A method as in claim 1 wherein the dispersion medium is water.

3. A method as in claim 1 wherein the dispersion medium is non-aqueous.

4. A method as in claim 1 wherein the dispersion medium is a combination of an aqueous and a non-aqueous medium.

5. A method as in claim 1 wherein the dispersion additionally contains a water repellent treating agent.

6. A method as in claim 1 wherein the insoluble Group II Metal salt is selected from calcium, zinc and magnesium.

7. A method as in claim 1 wherein the metal salt is selected from zinc oxide and calcium carbonate.

8. A method as in claim 1 wherein the metal salt is a combination of zinc oxide and calcium carbonate.

9. A method for treating wood to prevent the iron staining of the wood comprising applying to the wood a dispersion of a finely divided insoluble Group II Metal salt selected from the group consisting of beryllium, magnesium, calcium, strontium, barium, zinc, cadmium and mercury and wherein the dispersion medium is a combination of an aqueous and non-aqueous medium and wherein the dispersion additionally contains a water repellent treating agent.

10. A method for treating wood to prevent the iron staining of the wood comprising applying to the wood a dispersion of a finely divided insoluble Group II Metal salt selected from the group consisting of calcium, zinc and magnesium and wherein the dispersion medium is water.

11. A method as in claim 10 wherein the dispersion medium is non-aqueous.

12. A method as in claim 10 wherein the dispersion medium is a combination of an aqueous and non-aqueous medium.

13. A method as in claim 10 wherein the dispersion medium additionally contains a water repellent treating agent.

14. A method for treating wood to prevent the iron staining of the wood comprising applying to the wood a dispersion of finely divided insoluble Group II Metal salts selected from the group consisting of calcium, zinc and magnesium and wherein the dispersion medium is a combination of an aqueous and non-aqueous medium and wherein the dispersion medium contains a water repellent treating agent.

15. A method as in claim 14 wherein the metal salt is selected from zinc oxide and calcium carbonate.

16. A method as in claim 14 wherein the metal salt is a combination of zinc oxide and calcium carbonate.

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