

UNITED STATES PATENT OFFICE

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COPPER, CHROMIUM, ARSENIC COMPOUND
FOR WOOD PRESERVINGWilliam McMahon, Summit, N. J., assignor to Bell
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York, N. Y., a corporation of New YorkNo Drawing. Application December 31, 1941,
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10 Claims. (Cl. 167—38.5)

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This invention relates to preservative compositions for cellulosic material, such as wood; and the present application constitutes a continuation in part of my prior application, Serial No. 323,698, filed March 13, 1940 on Wood preservation, now abandoned.

The principal object of the invention is the provision of such a preservative composition that when applied to the cellulosic material it will not only preserve the material but will also result in a treated material of high insulation resistance.

Another object of the invention is to provide a water-borne preservative which when applied to cellulosic material, such as wood, forms no water-soluble salts.

A further object is to fix effectively and simultaneously in one operation compounds of copper, chromium and arsenic in wood or other material containing cellulose and lignin while avoiding the formation in the material of any permanently water-soluble salt.

In the preferred embodiment of the invention the wood preservative composition consists of an aqueous solution comprising chromic acid, arsenic acid and a compound of another metal such as copper, where the said copper compound consists of one or more of the following: copper hydroxide, copper carbonate, copper oxide, copper chromate, copper dichromate or copper arsenate. Copper dichromate is soluble in water while the other copper compounds mentioned are soluble in an aqueous solution of arsenic acid and chromic acid. Stated in a somewhat different manner, the preferred composition comprises a water-soluble compound of chromium, a compound of another metal such as copper, and if desired, a water-soluble compound of arsenic, where the compounds selected are of such a nature that when the wood is impregnated with an aqueous solution of these compounds in the proper proportions the reaction of certain substances in the wood with the impregnating solution results in the formation of new compounds, all of which are water-insoluble.

The feature of having all of the reaction products water-insoluble is of particular importance in the impregnation of telephone poles or other timber having galvanized iron or other metallic members affixed thereto. If the reaction between the wood and the impregnating solution

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is such as to form a new salt which is water-soluble, the insulation resistance of the pole would be decreased by the presence of such a compound; and if the new water-soluble compound is a salt, such as chloride or sulphate, the presence of such a salt would tend to accelerate corrosion of the pole line hardware.

For example, when an aqueous solution of chromium trioxide, copper hydroxide and arsenic pentoxide is injected into the wood the reaction of these compounds with the wood produces the following new compounds: chromium hydroxide, chromium arsenate, chromium chromate, copper arsenate, and copper chromate. All of these new compounds are insoluble in water and hence none of the new compounds is of such a nature as to increase the conductivity of the pole when subsequently exposed to moisture or running water; and, further, none of these new compounds tends to accelerate the corrosion of any metallic article affixed to the pole.

It has previously been proposed to employ certain chromium salts for the fixation of copper and arsenic in the wood to afford protection against wood-eating insects and wood-destroying fungi, where the fixation is believed to be due to the reduction of the chromate ions by certain substances in the wood. The present invention in that respect is similar to these earlier proposals but provides an improvement thereon particularly for those uses of the treated timber which require the attachment of metal fixtures to the timber, such as the hardware usually employed on telephone poles. Since the wood treated with the solution of this invention has a markedly higher electrical resistance than would be the case if the reaction of the ingredients on the wood produced a water-soluble by-product, it follows that the treated wood of this invention can also be advantageously used for poles for power transmission lines and the like.

In the above description of the preferred compositions, certain compounds of copper have been listed but, if desired, the corresponding compounds of nickel, zinc, cobalt or barium may wholly or partially replace the copper compounds. A further permissive variation is to omit the arsenic compound entirely where the fungi-destroying property of arsenic is not needed. It may also be noted that when the arsenic is added

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in the form of a metallic arsenate, the arsenic pentoxide may be absent or present in a correspondingly reduced amount; while when the major portion of the chromium is added in the form of a metallic chromate or dichromate it will still be advisable to add some chromium trioxide or its equivalent to produce chromic acid in the aqueous solution.

The following data include several examples of the preferred compositions of this invention and indicate in parts by weight the amount of each compound which is advantageous to employ, approximate upper and lower limits being given for each compound. In general, it may be stated that in the preferred wood preservative compositions of this invention each of the elements, chromium, arsenic and copper or other substituted metal, is present in sufficient amount to exert a substantial toxic action on wood-destroying organisms.

Example I

	Permissible Variation	Preferred
Arsenic pentoxide ($As_2O_5 \cdot 2H_2O$).....	5 to 15 parts....	Parts 5
Chromium trioxide (CrO_3).....	10 to 20 parts....	15
Copper hydroxide [$Cu(OH)_2$].....	6 to 9 parts....	6
Water.....	300 to 3000 or more parts.	

where the copper hydroxide may be replaced wholly or in part by the chemically equivalent weight of one or more of the hydroxides of zinc, nickel, cobalt or barium. For example, if the copper hydroxide of Example I is wholly replaced by zinc hydroxide ($Zn(OH)_2$) the permissible variation would be 6 to 9 parts with 6 parts preferred; if replaced by nickel hydroxide ($Ni(OH)_2$) the permissible variation would be 5.5 to 8.5 parts with 5.5 parts preferred; if replaced by cobalt hydroxide ($Co(OH)_2$) the permissible variation would be 5.5 to 8.5 parts with 5.5 parts preferred; or if replaced by barium hydroxide ($Ba(OH)_2 \cdot 8H_2O$) the permissible variation would be 19 to 29 parts with 19 parts preferred.

If desired, the copper hydroxide of Example I may be replaced by the chemically equivalent weight of any one of the other permissible copper compounds, as indicated by the subsequent examples:

Example II

	Permissible Variation	Preferred
Arsenic pentoxide ($As_2O_5 \cdot 2H_2O$).....	5 to 15 parts....	Parts 5
Chromium trioxide (CrO_3).....	10 to 20 parts....	15
Basic copper carbonate [$2CuCO_3 \cdot Cu(OH)_2$].....	7 to 11 parts....	8
Water.....	300 to 3000 or more parts.	

where the copper carbonate may be replaced wholly or in part by the chemically equivalent weight of one or more of the carbonates of zinc, nickel, cobalt or barium. For example, if the copper carbonate of Example II is wholly replaced by zinc carbonate ($ZnCO_3$) the permissible variation would be 7.5 to 12 parts with 8.5 parts preferred; if replaced by nickel carbonate ($NiCO_3$) the permissible variation would be 7 to 11 parts with 8 parts preferred; if replaced by cobalt carbonate ($CoCO_3$) the permissible variation would be 7 to 11 parts with 8 parts preferred; or if replaced by barium carbonate

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($BaCO_3$) the permissible variation would be 12 to 19 parts with 13.5 parts preferred.

Example III

	Permissible Variation	Preferred
Arsenic pentoxide ($As_2O_5 \cdot 2H_2O$).....	5 to 15 parts....	Parts 5
Chromium trioxide (CrO_3).....	10 to 20 parts....	15
Cupric oxide (CuO).....	5 to 7.5 parts....	5
Water.....	300 to 3000 or more parts.	

where the cupric oxide may be replaced wholly or in part by the chemically equivalent weight of one or more of the corresponding oxides of zinc, nickel, cobalt or barium. For example, if the cupric oxide of Example III is wholly replaced by zinc oxide (ZnO) the permissible variation would be 5 to 7.5 parts with 5 parts preferred; if replaced by nickel oxide (NiO) the permissible variation would be 4.5 to 7 parts with 4.5 parts preferred; if replaced by cobalt oxide (CoO) the permissible variation would be 4.5 to 7 parts with 4.5 parts preferred; or if replaced by barium oxide (BaO) the permissible variation would be 9.5 to 14.5 parts with 9.5 parts preferred.

Example IV

	Permissible Variation	Preferred
Arsenic pentoxide ($As_2O_5 \cdot 2H_2O$).....	5 to 15 parts....	Parts 5
Chromium trioxide (CrO_3).....	8 to 18 parts....	13
Basic copper chromate ($CuCrO_4 \cdot 2CuO \cdot 2H_2O$).....	7.5 to 11.5 parts....	7.5
Water.....	300 to 3000 or more parts.	

where the copper chromate may be replaced wholly or in part by the chemically equivalent weight of one or more of the corresponding chromates of zinc, nickel, cobalt or barium. For example, if the copper chromate of Example IV is wholly replaced by zinc chromate ($ZnCrO_4 \cdot 7H_2O$) the permissible variation would be 18.5 to 28 parts with 18.5 parts preferred; if replaced by nickel chromate ($NiCrO_4$) the permissible variation would be 10.5 to 16 parts with 10.5 parts preferred; if replaced by cobalt chromate ($CoCrO_4$) the permissible variation would be 10.5 to 16 parts with 10.5 parts preferred; or if replaced by barium chromate ($BaCrO_4$) the permissible variation would be 15 to 23 parts with 15 parts preferred. It also is to be noted that when the chromate of zinc, nickel, cobalt or barium is substituted for the basic copper chromate of Example IV, there is a slight change in the permissible variation of the chromium trioxide over the amounts given in Example IV, namely that the permissible amounts of chromium trioxide would become 5 to 15 parts, with 10 parts preferred.

Example V

	Permissible Variation	Preferred
Arsenic pentoxide ($As_2O_5 \cdot 2H_2O$).....	5 to 15 parts....	Parts 5
Chromium trioxide (CrO_3).....	0 to 8 parts....	3
Copper dichromate ($CuCr_2O_7 \cdot 2H_2O$).....	19 to 28.5 parts....	19
Water.....	300 to 3000 or more parts.	

where the copper dichromate may be replaced wholly or in part by the chemically equivalent weight of one or more of the dichromates of zinc,

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nickel, cobalt or barium. For example, if the copper dichromate of Example V is wholly replaced by zinc dichromate (ZnCr_2O_7) the permissible variation would be 17 to 25.5 parts with 17 parts preferred; if replaced by nickel dichromate ($2\text{NiCr}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$) the permissible variation would be 18 to 27.5 parts with 18 parts preferred; if replaced by cobalt dichromate ($\text{CoCr}_2\text{O}_7 \cdot \text{H}_2\text{O}$) the permissible variation would be 17.5 to 26.5 parts with 17.5 parts preferred; or if replaced by barium dichromate (BaCr_2O_7) the permissible variation would be 21 to 32 parts with 21 parts preferred.

Example VI

	Permissible Variation	Preferred
Arsenic pentoxide ($\text{As}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$)	0 to 10 parts	None
Chromium trioxide (CrO_3)	10 to 20 parts	15
Copper arsenate [$\text{Cu}_3(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$]	11 to 16.5 parts	11
Water	300 to 3000 or more parts.	

where the copper arsenate may be replaced wholly or in part by the chemically equivalent weight of one or more of the arsenates of zinc, nickel, cobalt or barium. For example, if the copper arsenate of Example VI is wholly replaced by zinc arsenate ($\text{Zn}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$) the permissible variation would be 12.5 to 19 parts with 12.5 parts preferred; if replaced by nickel arsenate ($\text{Ni}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$) the permissible variation would be 12 to 18 parts with 12 parts preferred; if replaced by cobalt arsenate ($\text{Co}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$) the permissible variation would be 12 to 18 parts with 12 parts preferred; or if replaced by barium arsenate ($\text{Ba}_3(\text{AsO}_4)_2 \cdot 3\text{H}_2\text{O}$) the permissible variation would be 15 to 23 parts with 15 parts preferred.

In the event that it is desired to fix only a compound of copper but not of arsenic in the wood the arsenic compound in the above examples may be omitted entirely, so that Example I, for instance, would become:

Example VII

Permissible variation

Chromium trioxide (CrO_3)	10 to 20 parts
Copper hydroxide [$\text{Cu}(\text{OH})_2$]	5 to 10 parts
Water	300 to 3000 or more parts

where the chromium trioxide and the copper hydroxide are preferably used in the ratio of 2 to 1 and where the copper hydroxide may be replaced wholly or in part by the chemically equivalent weight of one or more of the corresponding hydroxides of zinc, nickel, cobalt or barium.

The following remarks, as specifically applied to Composition I, are offered in explanation of the listing of preferred limits for the various ingredients employed in the wood preservative of this invention. As shown in Example I, the preferred limits for arsenic pentoxide are about 5 to 15 parts. Below about 5 parts the arsenic pentoxide is not present in sufficient amount to secure the desired effectiveness in wood preservation; while when substantially more than 15 parts are employed the arsenic is not so permanently fixed in the wood, as is the case when the amount employed is within the desired limits, and there

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would be an undesired leaching of the arsenic from the wood. With respect to copper hydroxide the same observations apply as for the arsenic compound. A minimum of about 6 parts of copper hydroxide is needed to secure the desired effectiveness in wood preservation; and when substantially more than 9 parts of copper hydroxide are employed the copper is not so permanently fixed in the wood as is the case when the amount employed is within the stated limits. The chromium compound is needed to cause the fixation of the copper and arsenic in the wood. The lower limit of about 10 parts of chromium trioxide is needed to maintain the arsenic and copper compounds in solution and precipitation will occur if a substantially smaller amount of chromium trioxide is employed. For the maximum amounts of the arsenic and copper compounds given in Example I, any amount of chromium trioxide beyond about 20 parts is unnecessary and superfluous in obtaining the desired fixation of the copper and arsenic compounds in the wood.

A composition of 5 parts arsenic pentoxide, 17 parts chromium trioxide and 6 parts copper hydroxide dissolved in 1000 parts of water has a pH value of 1.02.

The amount of water employed with the above compositions depends to some extent upon the type of treatment employed in impregnating the wood. In the "full cell" treatment, where the wood is first subjected to a partial vacuum and is then immersed in the solution under pressure for some time, the amount of water for the above examples should be in the neighborhood of 1000 to 2000 parts. In the so-called "empty cell" treatment, where the wood is first placed under greater than atmospheric pressure to drive air into the wood, and is then immersed in the solution under still greater pressure for a certain period of time, after which the wood is removed from the solution and placed under a partial vacuum, the solution employed should have a higher degree of concentration employing water in the neighborhood of 500 to 1000 parts.

It should be noted that the preservative composition of this invention can be safely used in iron or steel tanks or other wood-treating equipment without any objectionable corrosive action.

Several fungicides for treating wood telephone poles including the solutions of the present invention have been studied to determine their relative corrosiveness towards galvanized iron pole hardware with which they might come in contact. This was done by measuring the potential of iron immersed in the respective solution with a tenth normal calomel reference electrode by means of a continuously recording potentiometer where the readings were taken over a period of fifty minutes. In the following tabulation, solutions A and B are representative of this invention, while solutions C and D represent certain prior proposals.

Solution A consisted of:

	Parts
Copper hydroxide [$\text{Cu}(\text{OH})_2$]	10
Chromium trioxide (CrO_3)	17
Water	1000

Solution B consisted of:

	Parts
Arsenic pentoxide ($\text{As}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$)	5
Copper hydroxide [$\text{Cu}(\text{OH})_2$]	6
Chromium trioxide (CrO_3)	17
Water	1000

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Solution C was an aqueous solution of certain compounds of arsenic, copper and chromium where the compounds were such, when used as a wood preservative, as to produce a water-soluble sulphate as a by-product of the reaction of the solution with the wood; and the compounds used in this solution were those specifically preferred in a prior art proposal.

Solution D was also taken from the prior art and resembled solution C in that a water-soluble sulphate would be formed as a by-product in the reaction of the solution on the wood but differed from solution C by the omission of arsenic and the addition of a small amount of an organic acid.

Referring to the standard cell the initial potential of the iron in the various solutions and its potential after fifty minutes' exposure to the solution were as follows:

Solution	Initial Potential in Volts	Potential in Volts After 50 Minutes
A.....	-0.125	-0.03
B.....	-0.37	-0.315
C.....	-0.565	-0.470
D.....	-0.65	-0.66

From these data it is apparent that solutions A and B passivate the iron more strongly than solutions C and D since the potential values for solutions A and B are more electropositive than for solutions C and D. The formation of a passive film on the iron is indicated by the trend of the potential in the electropositive direction and by the magnitude of the potential change. From the standpoint of reducing corrosion, solutions A and B are therefore preferable to solutions C and D.

The insulation resistance of wood impregnated with solutions B, C and D has also been measured and from certain standpoints the more desirable solution is the one giving the wood the higher insulation resistance. In these tests of the insulation resistance, air-seasoned poles were treated with the various solutions and then were exposed in the open air for about eleven months before the following measurements were taken, where the insulation resistance given is in megohms per foot of test section length:

Solution	Insulation Resistance
B.....	1.7449
C.....	0.2053
D.....	0.2603
Standard creosote treatment.....	0.6582

The preservative of this invention may be injected into the wood in a variety of ways as by placing the wood under a partial vacuum and then immersing the wood in the solution under a pressure greater than atmospheric pressure; by the "empty cell" treatment previously described; or by dipping the wood in open vessels containing the preservative solution; or by brush or spray painting the wood with the solution.

After the preferred ingredients, arsenic pentoxide, chromium trioxide, and a copper compound such as copper hydroxide, are dissolved in water, the resulting solution may be considered as one containing arsenic acid, chromic acid and the copper compound; and hence in the following claims any reference to chromic acid or arsenic acid is also intended to include the oxide of

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chromium or arsenic. In further explanation of the language employed in some of the appended claims it may be noted that when arsenic pentoxide, chromium trioxide, and the oxide, hydroxide, carbonate, chromate, dichromate or arsenate of copper are dissolved in water, the solution consists substantially exclusively of ions of copper, ions of hydrogen, chromate ions, dichromate ions, and arsenate ions. It may also be noted that the copper, nickel, zinc, cobalt or barium compound employed in the solution of the present invention is preferably one in which the metal is divalent.

What I claim is:

15 1. A preservative for wood consisting of ingredients which, when dissolved in water, are capable of reacting with certain substances in said material to form compounds which are all water-insoluble, said ingredients comprising
20 chromium trioxide and a substantial amount of a copper compound the component of which, other than copper, is selected from the group consisting of hydroxide, carbonate, chromate, dichromate and arsenate, said chromium trioxide being present in a substantial amount at least
25 sufficient to maintain the metal compound in solution when the ingredients are added to water.

2. A wood preservative consisting of ingredients which, when dissolved in water, are capable of reacting with certain substances in the wood to form salts which are all water-insoluble, said ingredients comprising arsenic pentoxide, chromium trioxide and a copper compound in wood
35 preserving amounts, the component of the copper compound other than copper being selected from the group consisting of hydroxide, carbonate, chromate, dichromate and arsenate.

3. A wood preservative comprising an aqueous
40 solution of arsenic acid, chromic acid and a copper compound which is insoluble in water but is soluble in a water solution of arsenic acid and chromic acid, the component of said copper compound other than copper being selected from the
45 group consisting of hydroxide, carbonate, chromate, dichromate and arsenate, said arsenic acid, chromic acid and copper compound being present in sufficient amounts to exert a substantial toxic action on wood-destroying organisms.

4. A wood preservative consisting of an aqueous solution of chromium trioxide, copper hydroxide and arsenic pentoxide, where the ingredients are present in the following amounts by weight: approximately 10 to 20 parts of
50 chromium trioxide, approximately 6 to 9 parts of copper hydroxide and approximately 5 to 15 parts of arsenic pentoxide.

5. A wood preservative consisting of an aqueous solution of chromium trioxide, copper carbonate and arsenic pentoxide, where the ingredients are present in the following amounts by weight: about 10 to 20 parts of chromium trioxide, about 7 to 11 parts of copper carbonate and about 5 to 15 parts of arsenic pentoxide.

6. A wood preservative comprising by weight about 5 to 15 parts arsenic pentoxide, 10 to 20 parts chromium trioxide, and 6 to 9 parts copper hydroxide, where the amount of chromium trioxide employed is about twice the combined
70 amount of arsenic pentoxide and copper hydroxide.

7. A wood preservative comprising by weight about 5 to 15 parts arsenic pentoxide, 10 to 20 parts chromium trioxide and 7 to 11 parts copper carbonate, where the amount of chromium

trioxide employed is about twice the combined amount of copper carbonate and arsenic pentoxide.

8. An acidic impregnating solution for preserving wood which comprises a copper compound dissolved in an aqueous solution of arsenic acid and chromic acid, the component of the copper compound other than copper being selected from the group consisting of hydroxide, carbonate, chromate, dichromate and arsenate characterized in that when the wood is impregnated with the said solution, all of the compounds formed by the reaction of the solution with the wood are insoluble in water.

9. An acidic impregnating solution for preserving wood which comprises a metal compound dissolved in an aqueous solution of arsenic acid and chromic acid, characterized in that said metal compound comprises copper hydroxide and further characterized in that when the wood is impregnated with said solution all of the compounds formed by the reaction of the solution with the wood are insoluble in water.

10. An acidic impregnating solution for preserving wood which comprises a metal compound dissolved in an aqueous solution of arsenic acid

and chromic acid, characterized in that said metal compound comprises copper carbonate and further characterized in that when the wood is impregnated with said solution all of the compounds formed by the reaction of the solution with the wood are insoluble in water.

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REFERENCES CITED

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

UNITED STATES PATENTS

	Number	Name	Date
15	1,261,736	Ferguson	Apr. 2, 1918
	1,639,601	Gardiner	Aug. 16, 1927
	1,957,873	Wolman	May 8, 1934
	2,041,655	Gunn	May 19, 1936
	2,106,978	Kamesam	Feb. 1, 1938
20	2,139,747	Hager	Dec. 13, 1938
	2,149,332	Boller	Mar. 7, 1939
	2,194,827	Gordon	Mar. 26, 1940

FOREIGN PATENTS

	Number	Country	Date
25	198,825	Great Britain	June 14, 1923