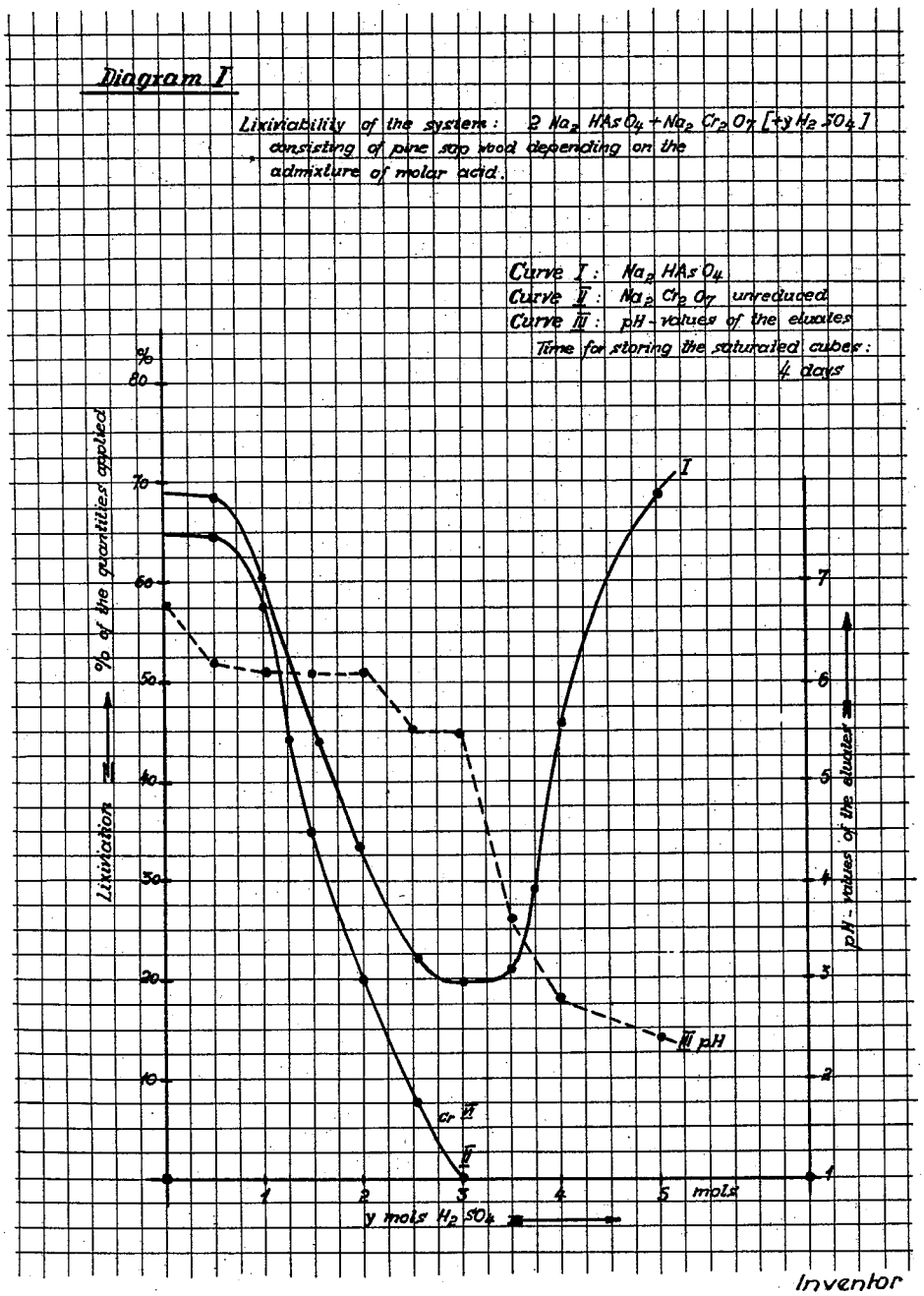
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WOOD IMPREGNATING COMPOSITIONS AND PROCESS

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WOOD IMPREGNATING COMPOSITIONS AND PROCESS

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This invention relates to wood-preserving impregnating agents, and more particularly to improvements in the compositions and the methods of impregnation of specific wood-preserving agents which comprise mixtures of salts which are well known in the art as Wolman salts, i.e. wood-preserving agents which are water-soluble compositions comprising for every two gram equivalents of a salt consisting of an anion containing hexavalent chromium and a monovalent cation, 6 *m* gram equivalents of a fluoride salt and *n* moles of an alkali arsenate, in which composition *m* plus *n* is equal to 2.

This invention is a continuation-in-part of my applications Serial No. 465,981, filed November 1, 1954, and Serial No. 593,041, filed June 22, 1956, both now abandoned.

The above-described water-soluble Wolman salts are also known in the art as "U" salts if they contain chromates and fluorides, and "UA" salts if they contain chromates and arsenates with or without the admixture of fluorides.

It is the principal object of my invention to provide wood preserving agents which are relatively non-lixiviable from the treated wood. These agents have a predetermined composition for achieving therewith a desired optimal effect of fixation in the wood depending upon the purposes for which the latter is to be used.

It is another object of my invention to provide a wood-preserving agent composition which permits a relatively close control of the velocity of fixation in the wood.

It is further object of my invention to provide a method of impregnating wood thereby, in the course of time, the entire wood including the core is penetrated by biocidal substances.

It is still another object of my invention to improve the impregnating effect of the known Wolman salts to permit their selective use for impregnating wood to be used as timber for a great variety of purposes.

These compositions of water-soluble salts of chromic acids, hydrofluoric acid and/or arsenic acid are applied in the art of preserving timber against destruction by vegetable and animal pests.

The fungicidal and/or insecticidal properties of these compositions are imparted to the wood over a longer period through the fact that the water-soluble components of these compositions react with the incrusting and other substances contained in the wood to form compounds of low solubility.

These reactions which take place in the wood comprise the reduction of hexavalent chromium to trivalent chromium and the formation of difficultly soluble or insoluble compounds of trivalent chromium with arsenic and/or fluorine, i.e. chromium cryolites and chromium (III) arsenates. They are generally called the "fixation of fluorides and arsenates" or the "fixation of Wolman salts" in the wood. It is, therefore, a typical feature of this fixation of Wolman salts that chromium participates in the fixation of both the fluorides and the arsenates.

It is generally accepted in the art that these fixation processes in wood are not complete, i.e. that a lagre percentage of the impregnating salts composition is lixiviated after treatment, for instance by immersion of the wood in water, by rain etc.

The degree of actually fixed amounts of these salts in the wood resulting from the known impregnation compositions, is subject to great fluctuations which were hitherto

ascribed to the different natures of the woods being impregnated. For example, in an article "The Invention of Wood Preserving U-Salts" by Dr. Joachim E. Koch, a pioneer and significant contributor to the development of the Wolman salts, published in "Chemiker-Zeitung, No. 10, May 20, 1954," it is stated that by treating sawdust with a U-salt mixture of 55 parts sodium fluoride and 35 parts potassium bichromate, about 70% of this mixture remained in the wood after exhaustive leaching. This U-salt was called "Triolith-U" or "Basilit-U," but when the same salts were employed on pieces of wood under actual conditions, it was discovered that only about 25% of the salt remained in the wood. The same type of experience was obtained with "Thanalith-U," a mixture consisting of 25 parts sodium fluoride, 25 parts sodium arsenate and 37 parts potassium bichromate, wherein the sawdust test showed that 90% was non-lixiviable, but in actual pieces of wood, only about 60% was non-lixiviable. It was, therefore, believed to be impossible to control generally and at will, the quantitative result as well as the velocities of these fixation processes in the wood.

It was further believed that the known compositions will not substantially corrode, if in the state of low concentration, as it is frequently required in the art of impregnating wood, and that these solutions could therefore be stored, for instance, in iron containers.

It has already been proposed in the art to add a very minor amount (1–2%) of preferably crystalline substances having an acid reaction, such as bisulfates, to compositions of approximately 1 mole alkali bichromate (sometimes called dichromate) and 2 moles alkali arsenate but with no fluoride. This is a UA Wolman salt free from fluorides so that in the above mentioned general formula of 6 *m* gram equivalents of a fluoride and *n* moles of an alkali arsenate, *m* must be zero. The pH of this composition in solution was, however, to be maintained at higher than 6. Consequently, complete precipitation of chromium (III) arsenate could not be achieved.

It is furthermore a known practice to add small quantities of citric acid or soluble salts of citric acid to impregnating salt compositions containing fluorine, chromium and arsenic, which admixture is said to prevent the formation of sludge which often occurs when working with this kind of preserving salt solution.

It has also been proposed in the art to produce wood impregnating agents by preparing mixtures of chromate or bichromate salts with potassium or ammonium bifluoride and/or arsenic compounds preferably with an admixture of other fungicides, insecticides, dyes and/or substances reducing the inflammability of the wood, in order to obtain salt compositions of particularly high solubility.

Therefore, it was thus far unknown in the art to prepare wood impregnating compositions which are adapted to preserve wood under very specific circumstances and uses. Finally, none of the known compositions, as a matter of fact, permitted the attainment of complete fixation. A complete fixation requires that substantially the entire amount of chromates, arsenates and/or fluorides originally applied to the wood remains therein and cannot be removed from the wood by lixiviation with water.

Check tests have also revealed that with the known compositions it is not possible to achieve a control of the fixation velocity in the wood. Thus, even an admixture of as much as 0.5 mole sulfuric acid to a composition of 2 moles alkali arsenate and 1 mole alkali bichromate would not substantially improve the fixing effect of the composition. Obviously, then, the proposed admixture of 2% H_2SO_4, corresponding to a molar admixture of only 0.14 mole H_2SO_4 is completely ineffective. When using bisulfates instead of sulfuric acid, the limiting concentration that must be exceeded, in order to

improve the fixation noticeably, is even higher than that concentration in the case of sulfuric acid, since bisulfates have to be considered the equivalents of monobasic acids only.

Because these various modifications of the Wolman salts did not lead to significantly different results, in commercial practice, the Wolman salts are supplied at a slightly alkaline pH. In other words, the effect of acid addition was considered unimportant and therefore a waste of money. As a matter of fact, the Koch article previously cited, on page 328, lines 17–27, states that during the chrome tests, it was singularly ascertained that bifluoride (e.g. NaFHF) did not influence the resistance to leaching of chrome.

In direct contrast to the teachings of the prior art, I have discovered that the addition of acid to a Wolman salt can greatly improve the resistance to lixiviation of the salts. As will be demonstrated hereinafter, the amount of acid that is added is critical, and this amount could not have been deduced by the teachings of the prior art. Whereas, a multitude of acids can be successfully utilized, it is preferred to utilize a member of the group comprising hydrofluoric acid, sulfuric acid, acetic acid, alkali bifluorides, alkali bisulfates, alkali pyrosulfates, ammonium salts such as ammonium sulfate or acetate or bifluoride, and mixtures thereof.

I have discovered that, when using these Wolman salt compositions for the impregnation of wood the quantity of monovalent cations such as potassium, sodium and/or ammonium is related only slightly to the type of wood being impregnated. This is so because the kinds of wood requiring impregnation contain, in nature, only very weak acids which acids, in fact, do not significantly influence the fixation processes in the wood. Of particular importance, it is essential to appreciate that whereas the prior art assumed the trivalent chromium ion to be bound in the form of insoluble fungicidal and insecticidal compounds, I have discovered that there are substantial quantities of non-lixiviable chromic compounds formed, free of arsenic and/or fluorine, e.g. chromic hydroxide, which have no fungicidal and/or insecticidal effect. These undesirable chromic compounds are formed due to the fact that there is insufficient acidity in the wood. On the basis of this fundamental discovery, I have taken one further step and have succeeded in formulating the reactions taking place in the wood and have also determined the ratios of the components in the composition required for optimal performance in treating various woods.

I have thus found that, when using the specific Wolman salt-containing compositons, the velocity and extent of fixation reaches an optimum when the converted Wolman salt contains at least one acidic substance which sets free some of the hydrogen ions in the Wolman salt solutions, and which shall be referred to hereinafter, for the sake of brevity, as proton donors. These proton donors must supply as many equivalent weights of hydrogen ions (protons) as are required for the complete neutralization of the above mentioned monovalent cations. That is to say, the hydroxyl ions associated with the alkali ions liberated from the starting compositions by the fixation and reduction processes in the wood, must be neutralized. On the other hand, if too much acid is added, the fixation products in the wood are dissolved.

In order to accomplish this neutralization, I have furthermore made a secondary discovery in that the weaker the acid used for neutralization, the lower the velocity of fixation; consequently, a control of the rate of fixation is possible.

I have found, as still another feature of my invention, that with neutral salts of hydrofluoric acid or arsenic acid (e.g. Na_3AsO_4) being present in the required molar ratios, in each case one should assume the reduction of only 1 mole alkali bichromate or only 1 mole alkali chromate, using respectively eight, or in the latter case, five equivalents of hydrogen ion. If, on the other hand, the arsenates are employed in the form of acid salts such as, for instance, Na_2HAsO_4, the fixation velocity will only reach optimal values if the number of hydrogen-ion equivalents necessary for the reduction of hexavalent chromium is decreased by certain minimum amounts which depend, for instance, on the content of acid hydrogen in the acid arsenates, independent of the reaction proper of the "acid arsenate" which may give in aqueous solution either an acid reaction or an alkaline one as is the case with Na_2HAsO_4.

In order to be able to compute the hydrogen-ion equivalents required for neutralizing the alkali ions set free in the wood in consequence of the reduction of chromate and/or bichromate and the fixation of arsenic and fluorine, it is necessary to know the chemical composition of the cryolites and of the chromic arsenate being formed during these processes.

I have discovered by experiments that the amount of acid required for the fixation process with "U"- and "UA" salts is such that the formation of $CrAsO_4$ and Me_3CrF_6 may be assumed. For example, a "UA"-salt composition comprising MeF, Me_2HAsO_4, and $Me_2Cr_2O_7$ shall be considered as a basis for computation. If, in order to facilitate the calculations, the symbol Hwd is used as indicating hydrogen as the reducing agent in the wood, and a monobasic acid HAc as indicating the proton donor in the process, the following formulae are obtained for the individual reaction steps:

(1) Bichromate-reduction:

$$Me_2Cr_2O_7+8HAc+6Hwd=2CrAc_3+2MeAc+7H_2O$$

One of the two Cr^{+++}-ions being formed will be consumed for the formation of cryolite, and the second for forming chromic arsenate. Me in the aforegoing and all the following formulae designates any kind of alkaline metal ion.

(2) Cryolite formation:

$$6MeF+CrAc_3=Me_3CrF_6+3.MeAc$$

(3) Chromic arsenate formation:

$$Me_2HAsO_4+CrAc_3=CrAsO_4+2MeAc+HAc$$

The sum reaction as obtained from combining Nos. 1 to 3, is expressed in Equation No. 4.

(4) $6MeF+Me_2HAsO_4+Me_2Cr_2O_7+7HAc+6.Hwd=Me_3CrF_6+CrAsO_4$ (fixed salts) $+7MeAc+7H_2O$

If m moles cryolite and n moles $CrAsO_4$ are to be formed from alkali arsenate, alkali fluoride and 1 mole alkali bichromate following the reduction process in the wood, then m plus n must be equal 2, because there are two Cr^{+++}-ions available. The amounts of reacting substances are then calculated on the basis of Equation No. 5:

(5) $m.6MeF+n.Me_2HAsO_4+Me_2Cr_2O_7+(8-n)HAc+6Hwd=m.Me_3CrF_6+n.CrAsO_4+(8-n)MeAc+7H_2O$

In the case of the composition discussed above and comprising di-alkali arsenate, monofluoride, and bichromate, the theoretically required amount of acid is equal to $8-n$ hydrogen ion equivalent.

If other components are chosen, then the theoretically required amount of acid may assume different values.

In the case of another example of a "UA"-salt system comprising MeF, Me_2CrO_4, and MeH_2AsO_4, the Equation No. 6 is obtained:

(6) $6m.MeF+n.MeH_2AsO_4+2Me_2CrO_4+(10-2n)HAc+6Hwd=m.Me_3CrF_6+n.CrAsO_4+(10-2n)MeAc+8H_2O$

In this example the theoretically required amount of hydrogen ion equivalent is $10-2n$.

As a further feature of my invention I have also discovered that the fixation velocity is greatest if approximately 0.75 to 1.2 times the theoretically required amount of hydrogen ion equivalent is used in the form of strong acids or their hydrogen salts for neutralizing the alkali ions being set free in the wood. In this case 1 mole of a strong acid, for instance a dibasic acid, corresponds to two hydrogen ion equivalents. It is to be decided in each case whether 0.75 or 1.2 times the theoretically required amount of hydrogen ion equivalents should be used for a certain determined combination of alkali chromates, or free chromic acid, alkali fluorides and/or arsenates with an acid, or whether another amount of acid between the aforesaid limits is to be added in order to obtain a minimum of lixiviability. This must be decided in each case experimentally on the basis of individual lixiviation tests.

If the hydrogen ion concentration (pH) is increased beyond the 1.2 fold amount, the reduction of bichromate or chromate will indeed take place very rapidly, but the lixiviability of the impregnated wood increases rapidly too. In the eluates from the lixiviation process chromium appears in its trivalent form.

On the other hand, if the hydrogen ion concentration decreases below the 0.75 fold amount, the quantitative degree of fixation may reach an optimum, if the acid content is not decreased too much below this value. However, the velocity of the chromate reduction and therewith the fixation process in the wood also decreases rapidly. In this case chromium appears in the eluates of lixiviation in its hexavalent and trivalent form.

I have thus discovered that, if an optimal fixation velocity is desired, hydrogen ion concentration should not be greater than the 1.2 fold amount and not less than the 0.75 fold amount of the theoretically required quantity.

According to another feature of my invention the progress with time of the fixation process, i.e. the fixation velocity, can thus be varied within broad limits by the following measures:

(1) According to a main feature of my invention the maximally required 0.75 to 1.2 fold amount of theoretically required hydrogen ion equivalents is added to the composition, or its solution.

When applying this step according to the invention, the reduction of Cr^{++++++} and the fixation of fluorides and/or arsenates will progress the slower, the weaker the acid used, i.e. the smaller its dissociation constant. It has also been found that fixation is slowed down if the ammonium salts of strong acids are used instead of the free strong acids, and if the valency of the acid anion is used as the basis for the computation of the hydrogen ion equivalents.

If, for instance, part of the required amount of hydrogen ions is obtained from ammonium sulfate and the rest from a strong acid such as H_2SO_4, or its hydrogen salts, then the fixation velocity may be varied between several days and several weeks according to the molar ratio chosen between ammonium sulfate and sulfuric acid. Apart from the ammonium salts of strong acids, any alkali compound may be used which is hydrolizable when brought into contact with water, and will form more or less strong acids, as will be the case with pyrosulfates.

(2) According to the invention, the hydrogen ion concentration is decreased below the 0.75 fold amount of theoretically required hydrogen ion equivalents. In this case the fixation process may also be quantitatively completed by using strong acids as proton donators, and lowering the hydrogen ion concentration to approximately 0.25 times the amount of theoretically required hydrogen ion equivalents. Fixation will then require considerably more time than when using the optimal hydrogen ion concentration. As can be seen from diagram I pertaining to Example I, the quantity of sulfuric acid chosen

in that example must exceed 0.5 mole, which is approximately 1 hydrogen ion equivalent, if a noticeable acceleration of the fixation of arsenic is to be achieved. Similar diagrams can be drawn up for all "UA"-compositions. Fixation will take place the more rapidly, the more the actual conditions approach the theoretically required hydrogen ion value.

However, the admixture of proton donor should not be reduced below 0.25 to 0.35 times the theoretically required amount, even when the proton donor is a strong or a relatively strong acid, i.e. an acid the dissociation constant of which is more than about 1×10^{-4}.

(3) According to a further feature of my invention, I provide rapidly fixing "UA"-compositions which are characterized by the fact that part of the fluorine introduced into the wood is capable of diffusion, i.e. it is not fixed.

This step is based on my discovery that the fixation of arsenic takes place more rapidly and more completely than the fixation of fluorine.

It had been unsuccessfully tried in the past to use arsenic acid as the proton donor for supplying the entire amount of acid required for the fixation of "UA"-compositions containing fluorine. These attempts failed because, as I have found, at least part of the arsenic acid destined for neutralizing the alkali ions set free in the wood by the fixation process, combines with chromium to form chromic arsenate, while at least part or all of the fluorine remains unfixed.

In other words, within the limits of the equation m plus $n=2$, only n moles must consist of arsenic acid. Arsenic acid must not be used for neutralizing the alkali ions set free by the fixation in the wood because this would lead to the conversion of the entire chromium present into chromium $^{+++}$ arsenate, so that no more chromium would be available for fixing the fluorine in the form of cryolite.

If arsenic acid is used as a neutralizing agent, about 95% of the fluorine will remain in lixiviable form while about 6% only of arsenic remain unfixed.

On the other hand, it is possible, due to the more rapid fixation of arsenic, to neutralize the excess of alkali ions set free in the wood by means of free hydrofluoric acid or by means of bifluorides, which neutralization leads to the formation of neutral fluorides (K_2F_2, Na_2F_2, or, possibly, $(NH_4)_2F_2$).

If there are sufficient potassium and/or sodium ions present in the form of alkali chromates and/or arsenates as are required in the preserving agent for a satisfactory cryolite formation, the proton donor added to the composition may be free hydrofluoric acid.

The share of unfixed fluorine may be regulated in different ways, for instance, by adding the acid destined for neutralizing the developing alkali, partly in the form of arsenic acid or its hydrogen salts, and partly in the form of other acids.

Apart from inorganic acids or substances capable of cleaving off inorganic acids, organic acids may also be used if they are not too rapidly oxidized by bichromates or chromates. The results discussed above under items 1 to 3 are also relevant if the respective "UA"- or "U"-compositions contain other adjuvants such as dinitrophenols, dinitrocresols and the like, besides chromium, fluorine and/or arsenic.

From an analysis of the preceding discussion it is believed that the novel wood-preserving agent of this invention can be best expressed as consisting essentially of $2/z$ moles of a chromate, $6m/f$ moles of an alkali fluoride, n moles of an alkali arsenate and $a(6+b-c)/d$ moles of acid wherein z is the number of chromium atoms in 1 mole of chromate; f is the number of fluorine atoms in 1 mole of fluoride; $m+n=2$; $a=0.25-1.2$; b is the number of alkali atoms being present as chromate; c is the number of H-atoms being present as anhydrous arsenate; and d is the valence of the acid.

The preceding formula for the ratio of components is more fully explained in the following remarks, and three examples, with particular emphasis directed to the meaning of the conditions $m+n=2$ and $a=0.25$ to 1.2.

The corresponding pairs of values of m, and $n=2-m$ can be freely selected. Their value determines only the extent to which the chromium content of the mixture in wood is converted to chromium cryolite (m mol) and chromium arsenate (n mol). Consequently, the selection of factors m and n depends solely on secondary factors, e.g. the intended use of the impregnated wood, on the corrosion properties of the impregnated wood upon certain metals or of the type of impregnating method which is to be used. For the construction of silos, for example, a certain wood is preferably impregnated with a mixture which is free or almost free from arsenic. As another example, wood which is in constant contact with pure aluminum will not be impregnated with a mixture acidified with much hydrofluoric acid because in the wood there are formed in addition to the difficulty soluble chromium cryolites, easily soluble alkali fluorides which attack pure aluminum (with the formation of Na_3AlF_6), especially in the presence of ammonium salts.

The acid content of the wood-preserving agent is determined by the factor a, which can also be freely selected within the specified limits. As stated previously, the acid content determines the fixing speed; consequently, the factor a is dependent on process considerations, primarily the particular method of impregnation and the type of wood being treated. For the Boucherie method, for example, rapidly fixing "UA"-salts cannot be used (i.e. a "UA"-salt whose chromium reduction in wood is completed in four days), because the Boucherizing takes a much longer time. On the other hand, woods which are subjected rapidly to severe conditions, such as in harbor constructions, are impregnated with a rapidly fixing salt. Furthermore, since the portions which are under water (posts) are attacked almost exclusively by animals and there is no danger of poisoning men, the arsenic content can be quite high in such cases.

EXAMPLE 1

The wood-preserving agent is to be used in the vacuum pressure method, for example, for impregnating woods for the construction of cooling towers. Because of the continuous water contact, the fluorine and arsenic components must be fixed as completely as possible. The wood-preserving agent to be acidified is comprised of $K_2Cr_2O_7$, NaF and KH_2AsO_4 and is acidified with sulfuric acid.

One mole $K_2Cr_2O_7$ contains 2 chromium atoms; consequently, $z=2$. According to the aforementioned formulation, there is in the wood-preserving agent

$$\frac{2}{z}=1$$

mole potassium bichromate which has 2 alkali atoms. Consequently, $b=2$.

It is desired that the chromium in the wood be converted predominantly to chromium cryolite; therefore, the following values are assumed:

$$m=1.2,\ n=2-1.2=0.8$$

Since the wood-preserving agent contains 0.8 mole KH_2AsO_4, there are 1.6 H-atoms present as anhydrous arsenate; consequently $c=1.6$.

One mole alkali fluoride contains 1 fluorine atom; therefore, $f=1$. Thus, the wood-preserving agent contains

$$\frac{6m}{f}=\frac{6(1.2)}{1}=7.2 \text{ mole NaF}$$

Therefore, the conventional, non-acidified wood-preserving agent has the following molar composition:

$$1K_2Cr_2O_7+7.2NaF+0.8KH_2AsO_4$$

The protective salt mixture has the following composition in percent by weight:

	Percent
NaF (practically 100%)	40.6
KH_2AsO_4 (98%)	19.8
$K_2Cr_2O_7$ (practically 100%)	39.6
	100.0

The figures in parentheses indicate the degree of purity of the used salts.

For the amount of added acid, it is seen that sulfuric acid is a bivalent acid; and therefore, $d=2$.

Factor a which controls the acid content of the wood-preserving agent is selected in such a way that a fixation with 3–4% impregnating solution is substantially completed four weeks after impregnation. Consequently factor a is selected to be 0.94.

The acid addition according to the invention is:

$$\frac{0.94(6+2-1.6)}{2}=3.0\ H_2SO_4$$

Forty grams of the unacidified wood-preserving agent are dissolved in about 500 g. water. Then, 31.68 g. sulfuric acid with a content of 50% H_2SO_4 are added to the aqueous solution. Then distilled water is added up to 1000 g. With this standardized solution, small blocks of pine sap wood ($5\times2.5\times1.5$ cm.^{3}) are impregnated according to DIN 52 176. The small blocks which are cut into small bars after impregnation were stored for twenty-eight days and then leached out according to the same standardized process. In the collected leaching waters, chromium, fluorine and arsenic were determined and were computed into percent of the quantities of Cr, F or As, respectively, applied to the wood. After a fixing time of twenty-eight days, the following solubilities were determined: 6% As, 44% F, 6% Cr.

In a second solubility experiment with the same concentration of solution and type of wood, a fixing time of forty-two days was used. In order to avoid excessively rapid drying, the impregnated, cut up, small bars remained in a closed container for four weeks and then were dried in the air for fourteen more days.

After a fixing time of forty-two days, the following solubilities were determined: 5% As, 41% F, 7% Cr.

As can be seen, this result is practically identical with the result obtained after a fixing time of four weeks.

By virtue of this example, it is obvious that solutions of conventional unacidified "UA"-salts can subsequently be provided with sufficient acid to increase the fixation of chromium arsenate and chromium cryolite with the substantial avoidance of chromium hydroxide formation. It is more convenient, of course, if the protective salt mixtures, as such, are suitably acidified and composed at the outset, which will be shown in the following Examples 2 and 3. These examples further show that the fluoride fixing time can be controlled to a large degree.

EXAMPLE 2

A slowly fixing wood-preserving agent is to be produced which is suitable for osmotic impregnating methods. In order to improve the speed of diffusion, the wood-preserving agent is to be acidified with excess hydrofluoric acid so that in the wood, besides a certain quantity of chromium cryolite (determined by factor m), neutral rapidly diffusing alkali fluorides are also formed.

As raw materials, there are used: Na_2CrO_4, $NAHF_2$ and K_2HAsO_4.

The composition of the wood-preserving agent is calculated as follows: 1 mole Na_2CrO_4, contains 1 chromium atom. Consequently, $z=1$, and the wood-preserving agent contains:

$$\frac{2}{z}=2Na_2CrO_4$$

One mole $NaHF_2$ contains 2 chromium atoms. Therefore $f=2$.

The 2 chromium atoms contained in the wood-preserv-

ing agent are desired to be changed in the wood at equal parts to chromium cryolite and chromium arsenate. Consequently $m=1$ and $n=1$.

Accordingly, the wood-preserving agent contains:

$$\frac{6m}{f}=\frac{6(1)}{2}=3NaHF_2$$

Also, the wood-preserving agent contains:

$$n=1K_2HAsO_4$$

Two moles alkali monochromate contain 4 alkali atoms; therefore, $b=4$.

One mole K_2HAsO_4 contains 1 hydrogen atom; therefore, $c=1$.

One mole bifluoride is, according to its acid content, a monobasic acid; therefore, $d=1$.

The acid content is

$$\frac{a(6+4-1)}{1}=a(9)$$

mole monobasic acid.

For the above named use, a favorable value for a is 0.50. Consequently, the wood-preserving agent must contain $0.5(9)=4.5$ moles monobasic acid. Three moles of $NaHF_2$ are already present in the wood-preserving agent, and therefore, another 1.5 moles $NaHF_2$ must be added.

The composition is as follows:

$$2Na_2CrO_4+3NaHF_2+K_2HAsO_4+1.5NaHF_2$$

or in weight percent:

	Percent
Na_2CrO_4 (98%)	39.4
$NaHF_2$ (97%)	34.2
K_2HAsO_4 (98%)	26.4
	100.0

The figures added in parentheses indicate the degree of purity of the used raw materials.

Standardized small blocks of pine sap wood were impregnated with a 4.00% solution of the wood-preserving agent, and were leached out as described in Example 1 after a fixing time of forty-two days. The solubilities were as follows: 7% Cr, 8% As, 47% F.

EXAMPLE 3

The protective salt mixture as described in Example 2 is to be produced from the same components and with the same fixing speed (with the same factor a) in such a way that the fluorine component completely changes to chromium cryolite in the wood. The wood-preserving agent is to be used for the Boucherie method. As acid component, $NaHSO_4$ is to be present in addition to sodium bifluoride which can also be considered a monovalent acid.

Therefore, the raw materials are: Na_2CrO_4, $NaHF_2$, K_2HAsO_4 and $NaHSO_4$.

Consequently, the values for z, f, m, n, a, b, c, and d are the same as in Example 2. The bifluoride arsenate and chromium content of the preserving agent being as follows:

$$2Na_2CrO_4+3NaHF_2+K_2HAsO_4$$

The acid content is also unchanged:

$$\frac{0.5(6+4-1)}{1}=0.5(9)=4.5$$

moles monobasic acid. Since the wood-preserving agent already contains 3 moles monobasic acid in form of $3NaHF_2$, it is necessary to add 1.5 moles sodium bisulfate. Therefore, the wood-preserving agent is composed as follows:

$$2Na_2CrO_4+3NaHF_2+K_2HAsO_4+1.5NaHSO_4$$

or in percent by weight:

	Percent
Na_2CrO_4 (98%)	35.8
$NaHF_2$ (97%)	20.8
K_2HAsO_4 (98%)	24.0
$NaHSO_4$ (practically 100%)	19.4
	100.0

The figures in parentheses indicate the degree of purity of the salts used.

Standardized small blocks of pine sap wood were impregnated with a 4.00% solution of the wood-preserving agent and were stored and leached out for forty-two days as described under Example 1. The solubilities were as follows: 8% Cr, 7% As, 39% F.

A comparison between the Examples 2 and 3 shows that the solubility of chromium and arsenic remained practicaly unchanged, whereas, the solubility of the fluoride decreased considerably. The lowest fluoride solubility which was observed in this test was around 35% F.

A further decrease in the fluoride content does not improve the fluoride solubility. The limiting values after leaching, however, increase because the fluorine content is not sufficient to change all the chromium to chromium cryolite. A part of the chromium then changes in the wood into chromium hydroxide which is fungicidally ineffective, and relatively soluble.

In general, the preservatives of this invention are utilized at strengths of about 1.5 to 10 weight percent in aqueous solutions.

To illustrate the marked superiority of the wood-preservatives of this invention as compared to prior art Wolman salts, the following test results are presented. In these tests, the Wolman "UA" and the Wolman "UAR" compositions are tabulated as follows:

"UA"

Moles:	Percent by weight
5.4 NaF	30
1.1 Na_2HAsO_4	28
1.0 $Na_2Cr_2O_7$	35
0.3 Dinitrophenol	7
	100

"UAR" 67

Moles:	Percent by weight
3 $NH_4F.HF$	28
$1KH_2AsO_4$	29
$1Na_2Cr_2O_7$	43
	100

According to the requirements of DIN 52176, page 2, ten blocks of pine wood were completely impregnated with 4% solutions of both of the salt mixtures submitted for testing. The degree of saturation was determined by analyzing the wood blocks before and after saturation. Immediately after saturation the blocks were separated into small sticks of about 3 mm. thickness. They were then loosely put into a glass container. This glass container remained covered for fourteen days with a glass plate and was then kept for fourteen more days while being opened off and on, and at the end was completely opened.

Then came the leaching. The little sticks of the ten blocks of each group were covered with 600 cc. of distilled water in a glass vessel and saturated. After one hour the liquid was poured off. The flask then remained standing with 600 cc. of distilled water, which was constantly renewed, for two hours, four hours the first day, eight hours the second day, eight hours the third day and seventy-two hours the fourth to the sixth day. Inbetween the wood blocks remained in closed containers without water.

The salt mixtures themselves and the leaching water were examined as to their content of fluorine and arsenic. In the fluorine determination, distillation was carried out and titration took place with thorium nitrate (Strache, F.: Holzforschung, 7, 1953, pages 111 to 116, and Berghoff, W. H., 11, 1957, pages 80 to 85) and in the arsenic determination, the operation was carried out according to the distillation method for 5-valence arsenic (E) Fischer Method, modified by M. Rohmer: BDC, GES., 34, 1901, pages 33 and 1565.

The chemical analysis of the leaching water are listed in Tables I and II for the fluorine and arsenic quantities leached out of the wood.

Table I

LEACHED OUT FLUORINE QUANTITIES

Leaching out		Leached out fluorine quantities [1]	
Sequence	Duration in hours	Wolman "UAR" 67, percent	Wolman "UA," percent
1	1	10.8	54.2
2	2	6.3	1.7
3	4	5.9	11.9
4	8	7.6	8.4
5	8	4.2	4.3
6	72	8.9	4.6
Total		43.7	[2] 101.1

[1] Flourine quantities expressed in percent of the fluorine absorbed by the wood upon saturation (impregnation).
[2] This result means that practically all fluorine has been leached out. In this connection the amounts above 100% are merely within the range of experimental error.

Table II

LEACHED OUT ARSEN IC QUANTITIES

Leaching out		Leached out fluorine quantities [1]	
Sequence	Duration in hours	Wolman "UAR" 67, percent	Wolman "UA," percent
1	1	0.7	10.8
2	2	0.6	4.1
3	4	0.2	3.9
4	8	0.6	4.3
5	8	0.3	2.0
6	72	1.2	3.3
Total		3.6	28.4

[1] Arsenic quantities expressed in percent of the arsenic absorbed by the wood upon impregnation (saturation).

Results.—The chemical examination of the leached waters according to DIN 52176, page 2, has shown that the resistance of wood impregnated with fluorine and arsenic is considerably greater with Wolman "UAR" 67 as compared to Wolman "UA."

Further tests were conducted to determine the toxicities of the salts with respect to insect larvae.

The examination was carried out according to DIN 52165. Pine blocks (dimensions 5 cm. by 2.5 cm. by 1.5 cm.) were impregnated completely with different dilutions of Wolman "UAR" 67 and Wolman "UA," whereby as solvent, distilled water was used. Subsequently, a portion of the little blocks was kept for four weeks at 20° C. and 75% relative humidity. The other portion was subjected to a so-called humid storage whereby the blocks were kept for two weeks in a container which was first closed, and slowly opened during the following two weeks.

Some of the blocks were subsequently subjected to a complete leaching out according to DIN 52176, page 2. This was a so-called stationary leaching out with two intermittent drying periods weekly. At the beginning of leaching out and after each drying period, the blocks were completely saturated with distilled water. The water was changed twice daily. The entire duration of leaching took four weeks. Thereafter into suitable holes in each little block ten egg larvae of the *Hylotrupes bajulus* L. were inserted. The animal experiments were carried out at 20° C. and 75% relative humidity. After four and twelve weeks the state of the larvae was determined after splitting the little blocks.

As the limit of toxicity of the salts, that concentration is given at which all animals were dead, or the next lower step where not all animals were dead. These two figures, in kg. to m.³ wood, are the toxic values of the salt solutions with respect to the larvae and the given testing time.

For control of the test conditions the untreated little blocks were used also in the same manner.

Results are shown in Tables III to VI.

Table III

Results of the testing of toxic effect of Wolman "UAR" 67 of "Hausbock-egg larvae" according to DIN 52165

Subjection of the treated little blocks	Drying of the treated little blocks	Duration of the animal tests in weeks	Content of Wolman "UAR" 67 in the impregnation solution in percent	Absorbed quantity of Wolman "UAR" 67 in kg. per m.³ wood	Condition of the larvae in percent of the stated animal test: Dead, Not inserted	Dead, Inserted	Living
Without leaching	Air drying	4	2	13	0	100	0
			1	6.5	0	100	0
			0.4	2.5	0	100	0
			0.2	1.2	0	100	0
			0.1	0.61	0	0	[1] 20
		12	0.1	0.61	0	100	0
			0.04	0.24	0	70	30
			0.02	0.12	0	20	80
			0.01	0.059	0	40	60
			Untreated comparison wood		0	0	100
	Humid storage	4	2	13	0	100	0
			1	6.4	0	100	0
			0.4	2.5	0	100	0
			0.2	1.2	0	0	[1] 20
		12	0.2	1.2	0	100	0
			0.1	0.61	0	100	0
			0.04	0.24	0	100	0
			0.02	0.12	0	70	30
			0.01	0.060	0	60	40
			Untreated comparison wood		0	0	100
With leaching	Humid storage	4	2	12	0	100	0
			1	6.2	0	100	0
			0.4	2.5	0	0	[1] 20
		12	0.4	2.5	0	100	0
			0.2	1.2	0	100	0
			0.1	0.62	0	40	60
			0.04	0.24	0	60	40
			0.02	0.12	0	40	60
			Untreated comparison wood		0	0	100

[1] The wood was not split to the end.

Table IV

Results of the testing of toxic effect of Wolman "UA" of "Hausbock-egg larvae" according to DIN 52165

Subjection of the treated little blocks	Drying of the treated little blocks	Duration of the animal tests in weeks	Content of Wolman "UA" in the impregnation solution in percent	Absorbed quantity of Wolman "UA" in kg. per m.³ wood	Condition of the larvae in percent of the stated animal test: Dead: Not inserted	Dead: Inserted	Living
Without leaching	Air drying	4	2	13	0	100	0
			1	6.5	0	100	0
			0.4	2.6	0	100	0
			0.2	1.3	0	100	0
		12	0.1	0.60	0	0	[1] 30
			0.1	0.60	0	100	0
			0.04	0.24	0	80	20
			0.02	0.12	0	30	70
			0.01	0.060	0	0	100
			Untreated comparison wood		0	0	100
	Humid storage	4	2	13	0	100	0
			1	6.4	0	100	0
			0.4	2.8	0	100	0
			0.2	1.3	0	0	[1] 20
		12	0.2	1.3	0	100	0
			0.1	0.60	0	100	0
			0.04	0.24	0	0	100
			0.02	0.12	0	10	90
			0.01	0.061	0	20	80
			Untreated comparison wood		0	0	0
With leaching	Humid storage	4	2	14	0	0	[1] 20
			2	14	0	90	10
			1	7.0	0	60	40
			0.4	2.8	0	70	30
		12	0.2	1.4	0	50	50
			0.1	0.65	0	0	100
			0.04	0.25	0	0	100
			0.02	0.13	0	10	90
			Untreated comparison wood		0	0	100

[1] The wood was not split to the end.

Table V

TOXIC VALUES OF WOLMAN "UAR" 67 WITH RESPECT TO "HAUSBOCK-EGG LARVAE" ACCORDING TO DIN 52165

Subjection of the treated little blocks	Drying of the treated little blocks	Duration of storage of the treated wood in weeks	Duration of the animal tests in weeks	Toxic values: In percent content of impregnation solution	Toxic values: In kg. protective means per m.³ wood
Without leaching	Air drying	19	4	0.1 -0.2	0.61-1.2
			12	0.04-0.1	0.24-0.61
	Humid storage	19	4	0.2 -0.4	1.2 -2.5
			12	0.02-0.04	0.12-0.24
With leaching	Humid storage	19	4	0.4 -1.0	2.5 -6.2
			12	0.1 -0.2	0.62-1.2

Table VI

TOXIC VALUES OF WOLMAN "UA" WITH RESPECT TO HAUSBOCK-EGG LARVAE" ACCORDING TO DIN 52165

Subjection of the treated little blocks	Drying of the treated little blocks	Duration of storage of the treated wood in weeks	Duration of the animal tests in weeks	Toxic values: In percent content of impregnation solution	Toxic values: In kg. protective means per m.³ wood
Without leaching	Air drying	19	4	0.1 -0.2	0.60-1.3
			12	0.04-0.1	0.24-0.60
	Humid storage	19	4	0.2 -0.4	1.3 -2.8
			12	0.04-0.1	0.24-0.60
With leaching	Humid storage	21	4	>2	>14
			12	≈2	≈14

To summarize the highly significant results of these tables:

Table I shows that the fluoride component of the old "UA"-salt has been completely washed out, whereas the fluoride component of "UAR" 67 was only washed out by 43.7%.

Table II shows that the arsenic component of Wolman "UA" was washed out by 28.4%, whereas the arsenic component could only be washed out by 3.6%, which data proves the improvement in fixation by this invention.

The last column of Table V shows that pine splint wood which was impregnated with 0.62 to 1.2 kg. "UAR" 67/m.³ was sufficiently protected against attacks of larvae after complete, standard washing.

Table VI (last horizontal column) shows that 14 kg./m.³ of the old "UA"-salt must be used to protect the wood to the same extent against larvae after equal, standard washing. It has thus been shown how to increase

the fixing of Wolman "UAR" 67 so much that only 1/10 of the protective substance is needed of what was required heretofore.

A further important feature of my invention is based on the surprising discovery that the lixiviability of fluorides is greatly reduced by the presence of both sodium and potassium ions together in the composition. I have found that the lixiviability of fluoride ion is particularly low if the composition or its solution contains, apart from the amount of acid required by this invention, at least one sodium ion per chromium atom as well as at least one, and, at will, more potassium ions.

This indicates that different types of cryolites are being formed, and further that the lixiviability of chromium and fluorine from woods which have been impregnated with salt compositions of the aforesaid kind is largely dependent, in spite of a complete reduction of bichromate, on the type of alkali ions chosen for these compositions.

If, for instance, pine wood is impregnated with a composition consisting of 7 moles potassium bifluoride, 1 mole alkali bichromate, and 1 mole potassium bisulfate, the lixiviability of chromium and fluorine in this case is, to a high degree, dependent upon whether chromium is used in the form of sodium bichromate or potassium bichromate. This is the more surprising since no essential differences can exist between the progress with time of the bichromate reduction, the concentration of hydrogen ions (pH) being the same in both cases.

Thus, if 20 to 70 percent of the alkali ions applied in the form of alkali bichromate or alkali monochromate, alkali fluoride and/or alkali arsenate consists of sodium ions, the lixiviability of the wood preserving agent from the wood impregnated therewith is further decreased.

That fluorine fixation in the wood may lead to different final products, as has been observed, is further indicated by the fact that iron corrosion can be extraordinarily dependent upon the sodium content of the compositions. Obviously coatings of different compositions are formed on the iron, which coatings resist the further attack by acids strongly in one case, but weakly in another.

At least one-tenth of the alkali ions applied in the form of alkali bichromate, or alkali monochromate, alkali fluoride and/or alkali arsenate should consist of sodium ions in order to reduce iron corrosion.

According to a still further feature of the invention the drawback of water soluble chromium-ammonia complexes being formed, is avoided by using salt compositions containing ammonium ions exclusively in mixture with sodium and potassium ions, and not alone. The use of some ammonium ion is per se desirable as it provides for reaction in which the wood contains, after impregnation, exclusively difficultly soluble chromium cryolites and chromium arsenates, but no other by-products which remain in the wood for a prolonged period, for the only by-products resulting in the following equation are ammonia and water.

$$4KF.HF+2NH_4F.HF+Na_2Cr_2O_7+6H= 2K_2NaCrF_6+2NH_3+7H_2O$$

Thereby the electric conductivity of the impregnated wood remains low or is greatly reduced over that of woods impregnated with compositions which leave as by-products easily soluble salts.

As yet another feature of the invention, wood is impregnated down to the center of the core by using specific compositions containing a certain amount of soluble, non-volatile fluorides capable of diffusion. The central part of a tree trunk, i.e. the core or xylem portion cannot be impregnated in healthy condition, but may subsequently be attacked by wood destroying fungi. Among these are the lentinus sqamosus and other lentinus species. Wood attacked by these fungi will become moist and water permeable.

The core wood or xylem can be impregnated by a method according to the invention and with a specific salt composition which contains fluoric acid or alkali bifluorides which entirely or partially neutralize the monovalent cations set free in the wood and form neutral fluorides therewith. Since the fixation of arsenic is much more rapid than the fixation of chromium and fluorine, a protective layer of difficultly soluble arsenates is formed in the outer strata of the wood, while the water soluble neutral fluorides remain inside this layer protected against lixiviation. As, in the course of time, the core of the wood becomes moist, these fluorides are capable of diffusing into the core or xylem and prevent growth of the above mentioned fungi therein.

Obviously, it would be of no advantage to introduce rapidly fixing salts into the wood by means of those known methods which rely, at the same time, on the diffusion of water-soluble salts. For instance, it can frequently be observed that the sap-conducting vessels of the wood (phloem) become gradually obstructed in particular by the very voluminous chromic arsenate during a process of sap displacement such as the Boucher method. In this case it would be more advantageous to compose the salt mixture or its solution in such a way that fixation does not take place too rapidly. On the other hand, the use for which the impregnated wood is destined often requires a fixation of the introduced preserving agents which is rapid and as complete as possible.

The lixiviability of "UA"- and "U"-salts is conventionally determined on the basis of standard tests one of which may be carried out as follows:

Small cubes of pine sap wood of predetermined dimensions are dried at 220° F., and weighed after cooling. Then they are saturated in vacuo with the solution to be tested, then dried externally and weighed again. The absorption of solution and/or preserving agent is computed from the weight difference. The cubes are then split into small sticks and are stored for a fortnight, in a covered vessel, then air-dried for another fortnight, and finally lixiviated. Lixiviation is carried out by quantities of 60 cc. water per original cube, the sticks being saturated therewith in vacuo. The water is renewed from time to time. Finally approximately 360 cc. will have been used per cube. The whole process of lixiviation lasts for seven days. The optimal values for lixiviation can thus only be obtained within the 28 days required for storing in the aforesaid standard test, if fixation by the "U"- or "UA"-salt in question has been completed within this time.

According to this standard test, it would correspondingly be sufficient to provide "U"- and "UA"-salts requiring a fixation period of less than 28 days. In practice, however, the preservation of wood has been improved in many cases if "U"- and "UA"-salts of a very slow fixation velocity are used instead of very rapidly fixing salts. This is, for instance, the case when impregnating, in particular, pine or fir wood by the vacuum pressure process, because this treatment usually leads to a low depth of penetration. After the impregnation proper, the preserving salts must be distributed through the wood by way of diffusion. However, this is not guaranteed when exclusively using rapidly fixing salts. The above described working procedure therefore comprises also preserving salt compositions of long fixation periods.

The following explanation will show in greater detail the various fields of wood treatment to which the compositions according to the invention can be applied.

Timber, which is to be used for underwater constructions, and in particular for port constructions, i.e. for constant submersion in sea water, must be treated with agents containing preferably arsenic and chromium compounds only or at least a large excess of arsenic over any fluorides present, because the fluorides are converted

by the calcium compounds present in the sea water into calcium fluoride which is, indeed, difficultly soluble, but is, on the other hand, ineffective as a fungicide or insecticide.

On the other hand, the presence of fluorine compounds in the wood is desirable in those portions of wooden structures which protrude above the water level, because the wooden portions not covered by water are, in the first place, subject to attack from wood-destroying fungi, while the wood portions below the water line are attacked by ocean fauna such as, for instance, *Teredo navalis* and Limnoria species, against which chromium (III) arsenate ($CrAsO_4$) is particularly active.

In contrast to the timber to be used in underwater construction, structural parts of timber which are to be used in living quarters, or in mining pits and galleries, or as wooden ties for railroads, must not be treated with preserving agents containing arsenic, because such wood may be used, after it has served any of the aforesaid purposes, as fuel. For certain fungi such as *Lencites trabea* and certain molds convert the arsenates in the wood into highly poisonous, gaseous arsenic hydride or organic arsines. When burning timber containing such arsenic compounds the smoke developed from the burnt material will contain arsenic oxide. Timber destined for the aforesaid purposes is, therefore, treated with arsenic-free wood-preserving agents.

While in the two above described cases the wood-preserving agent has to be selected to meet specific requirements, which make it necessary to use agents free from fluorine or free from arsenic, it is often desirable to work with impregnating salts, which contain, apart from hexavalent chromium, both fluorine as well as arsenic. Thus, wooden beams which are to be used, for instance, as telephone masts, must be introduced partly into the ground and partly stand above the same.

Due to the fact that, especially in soils rich in lime, fluorine may be converted partially or entirely to the non-biocide calcium fluoride, it is always necessary that the portions of the wood to be embedded in the soil are impregnated with agents containing not only fluorides but also arsenic. Arsenic and fluorides are highly effective not only against wood-destroying fungi but also against insects such as termites, larvae of *Hylotrupes bayulus* L. and other wood-destroying species.

Since it would be too expensive to apply one type of impregnation for the upper and another type for the lower part of beams destined, for instance, as telephone masts, impregnating agents are preferred which contain both fluorine and arsenic.

In order to illustrate the invention still further, the following examples are given which are, however, not intended to limit the invention.

In all of these examples where a certain amount of an alkali metal bichromate is mentioned as present in the prepared composition, such amount can, of course, be introduced either directly in the form of bichromate or in the form of a correspondingly high amount of monochromate which amount can easily be calculated on the basis of the stoichiometric ratios between the molecular weights of the monochromate and bichromate in question.

EXAMPLE IV

A wood-preserving composition is prepared for impregnating timber which is to be used for constructions under sea water.

In applying the equation:

$$(A)\ m.6MeF+n.Me_2HAsO_4+Me_2Cr_2O_7+(8-n)HAc+6H_{WD}=m.Me_3CrF_6+n.CrAsO_4+(8-n)MeAc+7H_2O$$

m is made equal to zero, i.e. n becomes 2 and the following reaction results:

$$(B)\ 2Me_2HAsO_4+Me_2Cr_2O_7+6HAc+6H_{WD}=2CrAsO_4+6MeAc+7H_2O$$

On the basis of this equation, which can be used according to the method of the invention, as an adequate basis for determining the components forming the desired composition, the latter is prepared adding as the proton donor fifty percent only of the required theoretical amount of hydrogen equivalents. Therefore:

3.36 kg. Na_2HAsO_4 (free from water)

and

2.64 kg. $Na_2Cr_2O_7.2H_2O$

are dissolved in about 100 liters of water, and 1.45 kg. crude concentrated H_2SO_4 (90%) are added thereto and the mixture diluted to a total volume of 200 liters. The resulting 3% solution of the composition according to the invention is used to impregnate a pine trunk, freshly cut and still containing cap, bast and bark by the Boucher process known per se. Approximately 2 cubic meters of wood can be impregnated with the above-stated amount of solution. The fixation requires about 4 to 5 weeks to be complete.

EXAMPLE V

In the aforesaid Equation A, given in Example IV, m is made equal 0.25 and n is, consequently 1.75. The disodium arsenate in the equation is replaced by monosodium arsenate and sodium bichromate by potassium bichromate. The equation then reads as follows:

$$6NaF+7NaH_2AsO_4+4K_2Cr_2O_7+18HAc+24H_{WD}=(Na,K)_3CrF_6+7CrAsO_4+18(Na,K)Ac+28H_2O;\ (Na,K)$$

indicates, in a conventional manner, that mixed crystals will be formed as far as the crystal structure permits.

80% of the theoretically required moles of proton donator are added in the form of H_2SO_4. The following composition results:

29.5 kg. HaF
133.5 kg. NaH_2AsO_4,

and

137.0 kg. $K_2Cr_2O_7$

which total of 300 kg. is dissolved in water; 92.4 kg. cruds H_2SO_4 (concentration 90%) are added thereto. The mixture is introduced into the storage container of vacuum pressure impregnating installation whose impregnation vessel has a capacity of 15 cubic meters, and the mixture in the storage container is then further diluted with water to a volume of 10,000 liters. Thereby a 3% solution of this composition according to the invention is obtained. The impregnating vessel is then charged with white-scaled dry pine wood, the vessel is evacuated to a vacuum of 20–30 Torr, and the solution from the storage container is then flooded into the vessel under vacuum. After pressure has been balanced, the solution begins to penetrate into the wood. An excess pressure period may follow as in the known process. Fixation requires 10 to 14 days to be complete.

EXAMPLE VI

In order to prepare a wood-preserving agent for the impregnation of timber that is to be used in building houses, the components of the Equation A in Example IV are so selected that n is equal zero, i.e. m is equal 2. The left side of Equation A then reads:

$$12KF+Na_2Cr_2O_7+8HAc+6H_{WD}$$

and by providing 7 moles HAc in the form of hydrofluoric acid H_2F_2 and the remaining mole of proton donators in the form of $NaHSO_4$, the Equation C is obtained as:

$$(C)\ 7KF.HF+5KF+Na_2Cr_2O_7+NaHSO_4+6H_{WD}=2K_3CrF_6+6KF+NaF+Na_2SO_4+7H_2O$$

By omitting the unreacted moles of potassium fluoride,

the Equation D is obtained, which corresponds to the reactions actually taking place in the wood:

(D) $7KF.HF+Na_2Cr_2O_7+NaHSO_4+6H_{WD}=2K_3CrF_6+KF+NaF+Na_2SO_4+7H_2O$

This equation also shows that Equation A can be used as the basic equation for computing all salt compositions according to the invention and that it can be readily adapted to all specific embodiments of compositions required for a specific impregnation purpose.

A composition prepared on the basis of Equation D is the following:

113.4 kg. KF.HF
61.8 kg. $Na_2Cr_2O_72H_2O$
24.8 kg. $NaHSO_4$ (anhydrous)

These 200 kg. of salt compositions are dissolved in water and introduced in the storage vessel of the vacuum pressure installation used in Example V. The solution in the storage vessel is then further diluted to a total volume of 10,000 liters, resulting in a 2% concentration of salts in the solution. White-scaled dry oak wood is then charged into the impregnating vessel of the apparatus and impregnated therein in a manner known per se. The fixation period is approximately 8 days.

EXAMPLE VII

A wood-preserving agent according to the invention is to be prepared which is particularly suited for impregnating timber to be used for general purposes, and, more particularly, for telephone or telegraph masts.

For this reason m in Equation A of Example IV is chosen equal 1, i.e. n is also equal 1. As an arsenic component anhydrous sodium meta-arsenate is to be used which is obtained from monosodium arsenate by dehydration, and is reconverted to the latter when being redissolved in water:

$$NaAsO_3+H_2O\rightleftharpoons NaH_2AsO_4$$

As an acid component, potassium bifluoride is used. Half the amount of the chromium-containing component consists of chromic acid. The acid content then corresponds to 72% of the theoretically required amount of hydrogen equivalents. The following Equation E results:

(E) $6KF.HF+2NaAsO_3+2CrO_3K_2Cr_2O_7+12H_{WD}=2K_3CrF_6+2CrAsO_4+2NaOH+2KOH+7H_2O$

A composition, prepared on the basis of this Equation E contains

37.3 kg. KF.HF
23.3 kg. $NaAsO_3$
23.4 kg. $K_2Cr_2O_7$
16.0 kg. CrO_3 present in the solution as H_2CrO_4

The 100 kilograms of this composition are then gradually added to a commercial paste-forming agent, for instance to a solution of 0.5 to 1 kilogram of the sodium salt of carboxymethyl cellulose in 15 liters of water, in a mixer provided with a motor-driven stirrer which is in operation during the mixing step.

The resulting paste may be further diluted with water to give it a desired consistency.

Sap-fresh pine poles are sealed white and then covered with the above paste, until 5 to 6 kg. of paste are applied per square meter of wood surface. The poles are then stacked closely packed and provided with a watertight cover such as bitumen cardboard. The stack is left standing for about 2–3 weeks. The salt has then deeply penetrated into the wood. After drying, the thus impregnated wood can be directly used for building porches, interior construction, telegraph poles and the like.

EXAMPLE VIII

This example shows the unexpected detrimental effect of an excess of arsenic present in the composition. According to the condition $m+n=2$, only n moles of arsensic should be present in the composition as arsenic acid. The alkali or ammonium ions set free in the wood by the fixation process must not be neutralized with arsenic acid, for the presence of the latter would impede the fixation of the fluorides.

I have formulated these reactions in the following equations:

(F) $6NaF+0.5As_2O_5+Na_2Cr_2O_7+1.25A_2O_5+6H_{WD}=Na_3CrF_6+CrAsO_4+2.5Na_2HAsO_4+1.75H_2O$

The cryolite and disodium arsenate react further with each other according to

(G) $Na_3CrF_6+Na_2HAsO_4=CrAsO_4+5NaF+NaF$

This shows that the entire fluorine remains in soluble form, and my tests have confirmed that about 95% of the fluorine can be removed from the wood by lixiviation after the fixation process is terminated. On the other hand, only 6% can be lixiviated, if lixiviation is carried out by the standard method described hereinbefore. A composition based on Equation F and comprising

26.4 kg. NaF
42.3 kg. As_2O_5
31.3 kg. $Na_2Cr_2O_7+2H_2O$

leads therefore only to the aforesaid highly unsatisfactory results.

EXAMPLE IX

This and the following Examples X and XI illustrate the neutralization of fluoric acid ions present in the wood-preserving composition either in the form of hydrofluoric acid or as bifluorides. The resulting neutral fluorides of monovalent cations [K_2F_2, Na_2F_2 or $(NE_4)_2F_2$] are protected against lixiviation from the impregnated wood by a surface layer of more rapidly and more completely precipitated (fixed) arsenic compounds, while these fluorides remain capable of diffusion into the xylene toward the core of the wood as aging of the latter proceeds.

In the reaction equation of Example VII, the resultant 1 mole of NaOH and 1 mole of KOH are successively neutralized with an alkali or ammonium bifluoride, such as for instance KF.HF. The following equation is obtained:

(H) $5KF.HF+NaAsO_3+CrO_3+0.5K_2Cr_2O_7+6H_{WD}=K_3CrF_6+CrAsO_4+3KF+(NaF+5.5H_2O)$

85% of the theoretically required acid is added to the following composition in the form of KF.HF and CrO_3

44.3 kg. KF.HF
20.7 kg. $NaAsO_3$
14.2 kg. CrO_3 present in the solution as H_2CrO_4
20.8 kg. $K_2Cr_2O_7$

The above 100 kg. of a Wolman salt composition are dissolved in water and the solution introduced into the storage container of a vacuum pressure apparatus and diluted therein to a total volume of 10,000 liters. A 1% solution is obtained. The impregnation vessel of the apparatus is charged with saw timber of pine wood which is impregnated in the vessel in the manner described in Example V. It is recommended to allow for an impregnation period of 1 to 2 hours, at an excess pressure of 5 to 6 atmospheres, after the pressure difference between storage container and vessel has been compensated. The fixation period requires from 10 to 14 days.

EXAMPLE X

Still more fluorine capable of diffusion is provided in the following equation:

(I) $5KF.HF+NaAsO_3+CrO_3+0.5K_2Cr_2O_7+6H_{WD}=K_3CrF_6+CrAsO_4+3KF+NaF+5.5H_2O$

100% of the theoretically required amount of proton donator are added in the form of KF.HF and CrO_3.

The composition is made up of:

49.8 kg. KF.HF
18.6 kg. $NaAsO_3$
12.8 kg. CrO_3 present in the solution as H_2CrO_4
18.8 kg. $K_2Cr_2O_7$

100.0 kg.

A 1% solution is prepared and used in the same manner as described in Example IX to impregnate saw timber of pine wood. The fixation period is only 6 to 10 days owing to the higher amount of acid added.

EXAMPLE XI

In the same manner as described in Example IX, a 1% solution is prepared; however, the amount of proton donator added is 71% of the theoretical value. Fir plants and boards are impregnated with the resulting solution in the same manner as described in Example IX. The fixation period is increased to two to three weeks.

EXAMPLE XII

Comparative lixiviation tests were made with pine sap wood blocks according to the standard testing method described in detail hereinbefore. The wood blocks were impregnated with 3% impregnating solutions of the compositions of Examples IX, X, and XI.

The lixiviability of chromium, arsenic, and fluorine is shown in Table 2.

Table 2

[In percent]

Example	Lixiviability of—		
	Cr	As	F
IX			45–49
X	6–10	8–11	55
XI			36–40

In all these lixiviation tests, the pH value of the eluates was between 4.8 and 5.2 and was determined with a foil-colorimeter of Wulff-Lautenschläger. This pH value corresponds to the natural pH value of pine sap wood determined in the eluates of non-impregnated block samples, and thus shows that all fluoric acid contained in the impregnating composition had actually been neutralized in the wood.

EXAMPLE XIII

The alkali bifluorides in the aforegoing examples may also be replaced by hydrofluoric acid, if there are present in the composition sufficient amounts of sodium and potassium ions in the form of alkalichromates and alkaliarsenates to satisfy the requirements of cryolite formation.

If, in accordance with $m+n=2$, m is chosen equal 1, and n is, consequently, equal 1, and Me is chosen as potassium and sodium, Equation A reads as follows:

(J) $5NaF+KF+KH_2AsO_4+Na_2Cr_2O_7+6HP+6H_{WD}=Na_2KCrF_6+CrAsO_4+5NaF+KF+7H_2O$

or written in abbreviated stoichiometric form:

(K) $KH_2AsO_4+Na_2Cr_2O_7+6HF+6H=Na_2KCrF_6+CrAsO_4+7H_2O$

A composition is correspondingly prepared from

30.1 kg. KH_2AsO_4
49.8 kg. $Na_2Cr_2O_7.2H_2O$
40.2 kg. H_2F_2 (50% concentration)

120.1 kg. total

The above 120.1 kg. of salt mixture is used in the form of a paste for a subsequent supplementary impregnation

of the particularly sensitive soil-air border zone of telephone poles already impregnated and plated in the soil.

In order to carry out this subsequent treatment a hole of about 2 feet depth is dug around the pole, the latter is cleaned with a brush from adhering soil, and about 450 grams of the paste are evenly spread over the mast surface in a zone extending from one foot below the soil surface level to 8 inches above the same. The pasted zone is covered with asphalted cardboard which is nailed on to the pole and sealed with bituminous paste about the top and bottom edges. The hole is then refilled with soil.

Lixiviation tests similar to those given in Example XII were made with a 4% solution of the above composition and with pine sap wood belocks of 5 x 2.5 x 1.5 centimeters, the 5 cm. edge being parallel to the fibers of the wood. 50–55% of the hydrofluoric acid applied to the wood had penetrated into the interior and remained therein. Furthermore, the electric conductivity of the wood decreased steadily in the course of 8 weeks.

The surprising decrease in the lixiviability of fluorine by a simultaneous presence of sodium and potassium ions in the impregnating composition is illustrated by Examples XIV, *a*, *b*, and *c*.

A composition is prepared which contains at least, apart from the required amount of proton donator, one gram atom of sodium for each gram atom of chromium, as well as a random number of gram atoms of potassium, but always, of course, at least one gram atom of K.

If, in Equation A and according to $m+n=2$, n is equal 0, m is, of course, 2. The required 8 moles of proton donator are added in the form of 1 mole of an alkali bisulfate and 7 moles hydrofluoric acid. The following general equation is obtained in which Me is either Na or K.

$$7MeF.HF+Me_2Cr_2O_7+MeHSO_4+6H_{WD}=2Me_3CrF_6+Me_2SO_4+2MeF+7H_2O$$

EXAMPLE XIV

(a) In the first of a series of three comparative tests, potassium alone is used as Me in Equation L and the following composition is obtained:

22.4 g. KF.HF
12.0 g. $K_2Cr_2O_7$
5.6 g. $KHSO_4$

40.0 g.

The 40 grams of total composition are then dissolved in distilled water in a polyethylene vessel and diluted further with distilled water to 1000 milliliters. The resulting 4% solution is used to impregnate standard blocks of pine sap wood as in Example XII, which blocks are then lixiviated according to the standard test supra.

(*b*) In the second comparative test, only sodium is used as Me in Equation L and the following composition is obtained and tested:

20.4 g. NaF.HF
14.0 g. $Na_2Cr_2O_7.2H_2O$
5.6 g. $NaHSO_4$

40.0 g.

(*c*) In a third comparative test, the preferred composition containing both sodium and potassium salts is prepared by mixing

22.7 g. KF.HF
12.3 g. $Na_2Cr_2O_7.2H_2O$
5.0 g. $NaHSO_4$

40.0 g.

Compositions (*b*) and (*c*) are used in the same manner as described for composition (*a*). The lixiviation results are compared in Table 3.

Table 3

LIXIVIABILITY OF CHROMIUM AND FLUORINE COMPONENTS IN PERCENT OF THE AMOUNTS CONTAINED IN THE STARTING COMPOSITION

Example	Lixiviability (in percent)	
	Cr	F
XIV (*a*)	84±1	88±5
XIV (*b*)	86±1	85±5
XIV (*c*)	17±0.5	31±2

EXAMPLE XV

Similar comparative tests as in Example XIV were made to show that lixiviability of fluorine is also drastically reduced when ammonium ions are present in the composition together with potassium and sodium ions, while compositions containing the ammonium ion together with only one of the alkali ions lead to impregnated timber from which practically the entire fluorine (up to 95%) can be lixiviated.

(*a*) In a first test, according to Equation A in which $m+n=2$ and $m=2$ (i.e. $n=0$), the fluoride salt used is neutral ammonium fluoride while as a proton donator, six moles of hydrofluoric acid are used, which corresponds to 75% of the theoretically required amount. On the basis of the resulting equation

(M) $6NH_4F.HF+K_2Cr_2O_7+6H_{WD}=2K(NH_4)_2CrF_6+2NH_4OH+5H_2O$

a composition is prepared which contains:

21.5 g. $NH_4F.HF$ and
18.5 g. $K_2Cr_2O_7$

40.0 g.

The composition is used for impregnating wood samples in the same manner as described in Example XIV.

(*b*) In a second test, a mixture of ammonium and potassium bifluoride is used replacing the fluoride component of test (*a*). Furthermore, sodium instead of potassium bichromate was used.

On the basis of the resulting equation

(N) $4KF.HF+2NH_4.HF+Na_2Cr_2O_7+6H_{WD}=2K_2NaCrF_6+2NH_4OH+5H_2O$

a composition is prepared which contains:

17.2 g. KF.HF
6.3 g. $NH_4F.HF$
16.5 g. $Na_2Cr_2O_7.2H_2O$

40.0 g.

All other conditions of this test including the addition of proton donator are the same as under (*a*). The results of both tests are compared in Table 4 below, which shows the lixiviability of the fluorine and chromium components in both cases, in percent of the amounts of these components in the compositions applied to the wood samples for impregnating the same.

In both tests the concentration of the impregnating solution is 4%.

Table 4

Example	Lixiviability (in percent)	
	Cr	F
XV (*a*)	85±1	90±5
XV (*b*)	15±0.5	25±2

The reason for the high lixiviability of wood impregnated with Composition XV (*a*) must be seen in the formation of the well-known, very stable but also easily water-soluble chromium-ammonia complex salts.

In Composition XV (*b*), the presence of both potassium and sodium causes the formation in the wood of cryolites having the formulae

K_2NaCrF_6 or $KNaCrF_5.H_2O$

which are very difficultly soluble and therefore show a small lixiviability.

The formation of these cryolites is confirmed by the fact that in Equations M and N the total amount of fluorine added (bifluoride component and proton donator) may be reduced from 12 to 10 gram atoms of fluorine without substantially changing the final results shown in Table 4.

The fact that the wood impregnated with Composition XV (*b*) contains, apart from the very difficultly soluble cryolites, only volatile compounds (ammonia and water), makes this composition particularly suited for impregnating railroad ties of beech, oak, pine and similar woods, whose natural electric conductivity should not be materially increased by impregnation, so that the electric signalling system may function unimpaired.

Thus a composition imparting to the wood an especially low electric conductivity is given in the following example:

EXAMPLE XVI

To the composition described under VII, an ammonium arsenate is added to further decrease the electric conductivity of wood impregnated therewith.

From a composition containing

5.0 g. KF.HF
4.8 g. $Na_2Cr_2O_7.2H_2O$
5.7 g. $(NH_4)_2AsO_4$
3.2 g. CrO_3 and 20 l. of water

there is prepared after adding 2.6 g. H_2F_2 (50%) a 1% solution with which small cubes of pine sap wood are vacuum impregnated. The sap wood cubes which are thus impregnated show after a storage period of 20 weeks an electric resistivity of less than ⅕ compared with the usual resistivity shown by wood treated with the known Wolman salt compositions under the same conditions. The water content of the impregnated and unimpregnated timbers was during measurement between 26 and 30%.

EXAMPLE XVII

A composition is prepared according to Example XIV (*c*) in which the sodium bisulfate is replaced by sodium pyrosulfate as an indirect proton donator.

The composition consists of

57.2 kg. KF.HF
31.2 kg. $Na_2Cr_2O_7.2H_2O$
11.6 kg. $Na_2S_2O_7$

When dissolving the composition, $NaHSO_4$ is formed from $Na_2S_2O_7$ and acts as a proton donator.

EXAMPLE XVIII

In order to show the effect of using a salt between a strong acid and a weak base, ammonium sulfate is used in the composition of Example XVII, which then consists of

60.1 kg. KF.HF
32.7 kg. $Na_2Cr_2O_7.2H_2O$
7.2 kg. $(NH_4)_2SO_4$

Finally, substances such as acid dyes may be incorporated into the compositions, according to this invention, which adjuvants make the impregnated wood uninflammable. Also, substances having highly fungicide properties such as chlorinated or nitrated phenols in quantities of 1 to 5% may be added thereto. All such adjuvants must, of course, be resistant to the chromate and/or bichromate ions in the composition.

It will be understood that while there have been given

herein certain specific examples of the practice of this invention, it is not intended thereby to have this invention limited to or circumscribed by the specific details of materials, proportions or conditions herein specified, in view of the fact that this invention may be modified according to individual preference or conditions without necessarily departing from the spirit of this disclosure and the scope of the appended claims.

What I claim is:

1. A wood-preserving composition containing a fluoride, a chromate, and an arsenate in the proportions of $2/z$ moles of a chromate, $6\ m/f$ moles of an alkali fluoride, n moles of an alkali arsenate, and $a(6+b-c)/d$ moles of an acid where z is the number of chromium atoms in the chromate molecule, f is the number of fluorine atoms in the fluoride molecule, $m+n=2$, a is any value from 0.25 to 1.2, b is the number of alkali atoms in the chromate molecule, c is the number of hydrogen atoms in the molecule of anhydrous arsenate, and d is the valence of the acid, the composition being substantially free from Cu, Zn, Ca and Mg compounds.

2. The composition of claim 1, in which the specified ingredients are respectively NaF, $K_2Cr_2O_7$, and KH_2AsO_4.

3. The composition of claim 1, wherein the acid is H_2SO_4.

4. The composition of claim 1 containing a fluoride, a chromate, and an arsenate, and in which the fluoride is present in larger amount by weight than the arsenate.

5. The composition of claim 1 containing a fluoride, a chromate, an arsenate, and a bisulfate, and in which the fluoride is present in larger amount by weight than the arsenate.

6. A process for preserving wood in which the wood is treated with the composition of claim 1.

7. A process for preserving wood in which the wood is treated with the composition of claim 2.

8. A process for preserving wood in which the wood is treated with the composition of claim 3.

9. A process for preserving wood in which the wood is treated with the composition of claim 4.

10. A process for preserving wood in which the wood is treated with the composition of claim 5.

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