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WOOD PRESERVING COMPOSITIONS

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This invention is concerned with improvements in or relating to wood preservative compositions in powder form and is more particularly concerned with such wood preservatives as contain copper and/or zinc sulphate.

The use of copper sulphate in wood preservatives is well known and in particular the use of compositions containing copper sulphate penta-hydrate and an alkali metal dichromate has been proposed. It has also been proposed to use zinc sulphate heptahydrate in place of the copper sulphate penta-hydrate. Such compositions also may contain arsenic compounds such as arsenic pentoxide.

The use of copper sulphate, in the form of its penta-hydrate has, however, been found to give rise to various difficulties, particularly in the satisfactory manufacture, storage and use of a powdered wood preservative mixture; thus powdered compositions containing copper sulphate penta-hydrate, an alkali metal dichromate and arsenic pentoxide in general take up moisture rapidly from the atmosphere and an initially dry and free flowing mixture of the components soon becomes pasty and may eventually become liquid. Furthermore, an initially dry mixture of these three components is not stable, in the physical sense, on prolonged storage, even when packed in air-tight containers, and can become virtually impossible to handle satisfactorily, even after a short storage period. Not only are the handling difficulties increased but the health hazards associated with the removal of the preservative from the container are likewise increased. Similar difficulties are encountered when using zinc sulphate in the form of its hepta-hydrate.

The reason for this change in state has been traced to the interchange of water between compounds with loosely combined water (as water of crystallization), for example copper sulphate penta-hydrate, and the very deliquescent arsenic pentoxide.

By "compounds with loosely combined water" we mean compounds such as copper sulphate penta-hydrate or zinc sulphate hepta-hydrate which can lose a proportion of their water of crystallization at temperatures of for example about 20° C., and particularly at temperatures of 35–40° C., that is temperatures which can be experienced in tropical or sub-tropical areas, in which the preservative might either be stored or through which it might be transported. In the presence of a deliquescent compound such as sodium dichromate or arsenic pentoxide the loss of water from, for example, copper sulphate penta-hydrate or zinc sulphate hepta-hydrate is accelerated with the result that the mixture will agglomerate or become a paste.

As a result, the use of such compositions containing mixtures of penta-hydrated copper sulphate and/or zinc sulphate hepta-hydrate together with chromates and/or dichromates and arsenic have not been developed to any great extent, although there are clear indications that such preparations would be advantageous from a preservative point of view. Previously the above-mentioned disadvantages have been reduced to some extent by obtaining

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the several ingredients separately and making up the preservative at the time of use. Such a practice is, however, inconvenient and may, inter alia, give rise to incorrect mixing of the ingredients and hence poor treatments. A further disadvantage is that the plant operator may be exposed to the health hazards associated with the use of the arsenic pentoxide either in solid or liquid form. Again these disadvantages have also been reduced in part by manufacturing a concentrated solution. Such a procedure offers certain problems of storage and the concentrated solution is not as easy to handle as the free flowing powder at the treatment plant. Moreover, the handling of a concentrated liquid containing arsenic pentoxide has been found to subject the plant operator to health hazards.

It is an object of the present invention to provide a wood preservative composition containing copper sulphate and/or zinc sulphate in the form of a free flowing powder wherein the above-mentioned disadvantages are reduced and which remains for a reasonable time, in a form which can be more readily handled, particularly at the treatment plants, than hitherto known compositions containing copper sulphate and/or zinc sulphate.

Our investigations have shown that if copper sulphate, usually present in powdered wood preservative compositions as the penta-hydrate is dried down to the form corresponding to a total moisture content equivalent to three molecules of water of crystallization or to a lower state of hydration, it may conveniently be used in the manufacture of solid wood preservative compositions in powder form with improved results from the above-mentioned points of view.

Copper sulphate in the form corresponding to a total moisture content equivalent to three molecules of water of crystallization or in a lower state of hydration may conveniently be prepared by heating the penta-hydrate for a prolonged period at an elevated temperature, for example 40° C.

We prefer to employ a copper sulphate which has been dried substantially to the form of the mono-hydrate, that is $\text{CuSO}_4 \cdot \text{H}_2\text{O}$, and containing not more than 10% excess (over theoretical $1\text{H}_2\text{O}$) of water as determined by the method of Dean and Stark using toluene as the refluxing medium.

Our investigations have also shown that if zinc sulphate, usually present in powdered wood preservative compositions as the hepta-hydrate is dried down to a form corresponding to a total moisture content equivalent to three molecules of water of crystallization or to a lower state of hydration, it may also conveniently be used, with advantage, in the manufacture of solid wood preservative compositions.

We prefer to employ a zinc sulphate which has been dried substantially to the form of its monohydrate, that is $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ and containing not more than 10% excess (over theoretical $1\text{H}_2\text{O}$) of water as determined by the method of Dean and Stark using toluene as a refluxing medium. The method of determining water referred to herein as the method of Dean and Stark is described in British Standard Institution Specification No. 756, dated 1939, entitled "Apparatus for Determination of Water by Distillation With an Immiscible Liquid."

Accordingly the invention comprises a wood preservative composition in a powdered free flowing form adapted to be dissolved in water prior to use for wood preservation comprising in admixture copper sulphate and/or zinc sulphate each in a form corresponding to a total moisture content equivalent to three molecules of water of crystallization or to a lower state of hydration, together with one or more of the following substances, namely, potassium dichromate, ammonium dichromate and anhydrous sodium dichromate.

It is preferred that the wood preserving compositions according to the invention should not contain any deliquescent compounds.

The term "deliquescent" used herein is used to designate such compounds for example as arsenic pentoxide or sodium dichromate which can absorb moisture from the surrounding atmosphere to such an extent that they can become liquified.

Where the wood preserving composition contains arsenic we prefer that this be in the form of a "low pH alkali arsenate free flowing powder" of the type described in applicant's co-pending application No. 522,366, filed July 15, 1955 and now Patent No. 2,816,057, issued December 10, 1957, which term when used therein means an alkali metal or ammonium arsenate, preferably a sodium arsenate, which in 1.2% w./v. aqueous solution gives rise to a pH of less than 4.6 and preferably less than 3.6, but not less than 2.0. The symbol w./v. indicates weight/volume on the metric scale.

Various grades of "low pH alkali arsenate free flowing powder" can be prepared and we prefer to employ a low pH sodium arsenate free flowing powder containing from 60-70% by weight of combined arsenic calculated as arsenic pentoxide (As_2O_5) based on an oven dry weight at 100° C. It is to be noted that it may be desirable to add to the low pH alkali arsenate free flowing powder, during its manufacture, or at a later stage, various diluents in order to regulate the characteristics, such as the pH and consistency, of the final product. Thus it has been found to be advantageous to add sodium sulphate to the low pH sodium arsenate free flowing powder to facilitate grinding. The incorporation of sodium bisulphate has also been found to be advantageous in facilitating the production of a free flowing powder and for regulating the pH of the preservative composition.

Whilst it is preferred that the arsenic be in the form of a "low pH alkali arsenate free flowing powder" the arsenic can be incorporated in the wood preserving composition in the form of arsenic pentoxide.

Alkali metal dichromates which can be used in the manufacture of wood preserving compositions include the dichromates of potassium and sodium; of these we prefer to use potassium dichromate. The use of anhydrous sodium dichromate offers certain disadvantages. Thus a mixture comprising arsenic pentoxide or "low pH alkali arsenate free flowing powder," anhydrous sodium dichromate and mono-hydrated copper sulphate (containing not more than 10% excess water determined by the method of Dean and Stark) can be stored for a reasonable length of time in air-tight containers. Once, however, the product is exposed to the atmosphere it agglomerates and liquifies and becomes difficult and hazardous to handle. If however the anhydrous sodium dichromate is replaced by potassium dichromate the preservative shows a reduced rate of agglomeration or none at all according to whether the "low pH alkali arsenate free flowing powder" or arsenic pentoxide be used and according to the proportion of arsenic pentoxide used.

In the compositions of the invention potassium dichromate and anhydrous sodium dichromate can be used. Thus if circumstances enforce the use of sodium dichromate either separately or in admixture with potassium dichromate in compositions according to the invention, increased stability of the powder when stored in air-tight containers is obtained provided that the sodium dichromate is used in its anhydrous state. It must be understood however that compositions containing sodium dichromate do not remain physically stable for any period once exposed to the atmosphere.

A wood preserving composition according to the present invention may also contain other compounds which may have a preserving action. Such compounds are, for example, sodium hydrogen fluoride, dinitrophenol and the cresols.

The compositions according to the invention are preferably such as have in aqueous 4% solution a pH within the range of from 2.0-2.8, preferably 2.1-2.25.

Preferred wood preserving compositions according to the invention include, for example, a composition comprising a low pH sodium arsenate free flowing powder, copper sulphate mono-hydrate (containing not more than 10% excess water as determined by the method of Dean and Stark) and potassium dichromate, see Example No. 1; copper sulphate mono-hydrate (not more than 10% excess water by the method of Dean and Stark) and potassium dichromate, see Example No. 2; a composition comprising copper sulphate mono-hydrate (not more than 10% excess water by method of Dean and Stark) potassium dichromate, sodium hydrogen fluoride and dinitrophenol, see Example No. 3; a composition comprising zinc sulphate mono-hydrate (containing not more than 10% excess water as determined by the method of Dean and Stark), potassium dichromate and low pH sodium arsenate free flowing powder see Example No. 5; and a composition comprising zinc sulphate (containing 17% excess water as determined by the method of Dean and Stark) potassium dichromate and arsenic pentoxide. Such preservatives will in general remain reasonably stable when exposed to the atmosphere and stable as free flowing powders when packed in air-tight containers for several months.

A specific preferred wood preserving composition according to the invention which will remain stable for several weeks in a temperate climate when packed in air-tight containers but will agglomerate and pastify when exposed to the atmosphere is one containing copper sulphate mono-hydrate (containing not more than 10% excess water as determined by the method of Dean and Stark) anhydrous sodium dichromate and arsenic pentoxide (see Example No. 4).

In order that the invention may be well understood the following examples are given by way of illustration only:

Example No. 1

A composition was made up as follows:

	Percent
Copper sulphate mono-hydrate (containing 10% excess water as determined by the method of Dean and Stark).....	27
Potassium dichromate.....	45
Low pH sodium arsenate free flowing powder—pH 2.1, 67% $As_2O_5 \cdot 2H_2O$ content (containing sodium bisulphate).....	28

This composition remained as a reasonably free flowing powder when stored in air-tight containers for considerable periods, and could be exposed to atmospheric moisture pick-up for a reasonable period without serious caking or agglomeration.

Example No. 2

A composition was made up as follows:

	Percent
Copper sulphate mono-hydrate (containing 10% excess water as determined by the method of Dean and Stark).....	43.5
Potassium dichromate.....	56.5

This composition remained as a reasonably free flowing powder when stored in air-tight containers for considerable periods under tropical conditions, and could be exposed to atmospheric moisture pick-up for a reasonable period without serious caking or agglomeration.

Example No. 3

A composition was made up as follows:

	Percent
70 Copper sulphate mono-hydrate (containing 10% excess water as determined by the method of Dean and Stark).....	36.5
Potassium dichromate.....	50.5
Sodium bifluoride.....	9.5
75 Dinitrophenol.....	3.5

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This composition remained as a free flowing powder when stored in air-tight containers and could be exposed to atmospheric moisture pick-up for a reasonable period without serious caking or agglomeration.

Example No. 4

A composition was made up as follows:

	Percent
Copper sulphate mono-hydrate (containing 10% excess water as determined by the method of Dean and Stark).....	27
Anhydrous sodium dichromate.....	50
Arsenic pentoxide ($As_2O_5 \cdot 2H_2O$).....	23

This composition remained as a reasonably free flowing powder when stored in air-tight containers for a reasonable length of time under tropical conditions but picked up water at a rapid rate when exposed to the atmosphere.

Example No. 5

A composition was made up as follows:

	Percent
Zinc sulphate mono-hydrate (containing 10% excess water as determined by the method of Dean and Stark).....	27
Potassium dichromate.....	45
Low pH sodium arsenate free flowing powder (pH 2.1, 67% $As_2O_5 \cdot 2H_2O$ content; containing sodium bisulphate).....	28

This composition remained as a free flowing powder when stored in an air-tight container, in tropical conditions, for a reasonable length of time and could be exposed to atmospheric moisture pick-up for a reasonable period without serious caking or agglomeration.

Example No. 6

A composition was made up as follows:

	Percent
Zinc sulphate (containing 17% excess water as determined by the method of Dean and Stark and corresponding approximately to $ZnSO_4 \cdot 2H_2O$).....	29
Potassium dichromate.....	48
Arsenic pentoxide.....	23

This composition remained as a free flowing powder when stored in an air-tight container for a reasonable time but was not as stable as the composition described in Example No. 1. The material slowly agglomerated when exposed to the atmosphere.

Example No. 7

A composition was made up as follows:

	Percent
Copper sulphate trihydrate.....	27
Potassium dichromate.....	45
Low pH sodium arsenate free flowing powder—pH 2.1; 67% $As_2O_5 \cdot 2H_2O$ (containing sodium bisulphate).....	28

This composition remained as a reasonably free flowing powder when stored in air-tight containers for considerable periods.

Example No. 8

A composition was made up as follows:

	Percent
Ammonium dichromate.....	45
Copper sulphate mono-hydrate (containing 10% excess water as determined by the method of Dean and Stark).....	27
Low pH sodium arsenate free flowing powder—pH 2.1; 67% $As_2O_5 \cdot 2H_2O$ (containing sodium bisulphate).....	28

This composition remained as a free flowing powder for a considerable period when stored in air-tight containers.

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I claim:

1. A wood preservative composition in a powdered free flowing form adapted to be dissolved in water prior to use for wood preservation comprising in admixture a member of the group consisting of arsenic pentoxide and water soluble arsenates, a member of the group consisting of copper sulphate and zinc sulphate in a form corresponding to not more than a total moisture content of three molecules of water of crystallization, and a member of the group consisting of potassium dichromate, ammonium dichromate and anhydrous sodium dichromate.

2. A wood preservative composition in a powdered free flowing form adapted to be dissolved in water prior to use for wood preservation comprising in admixture a member of the group consisting of arsenic pentoxide an alkali metal and ammonium arsenates which in 1.2% w./v. aqueous solution give a pH of less than 4.6, a member of the group consisting of copper sulphate and zinc sulphate in a form corresponding to not more than a total moisture content of three molecules of water of crystallization, and a member of the group consisting of potassium dichromate, ammonium dichromate and anhydrous sodium dichromate.

3. A wood preservative composition in a powdered free flowing form adapted to be dissolved in water prior to use for wood preservation comprising in admixture a member of the group consisting of arsenic pentoxide and alkali metal and ammonium arsenates which in 1.2% w./v. aqueous solution give a pH of less than 4.6, a member of the group consisting of copper sulphate and zinc sulphate containing not more than 10% excess water, over theoretical $1H_2O$, and a member of the group consisting of potassium dichromate, ammonium dichromate and anhydrous sodium dichromate.

4. A wood preservative composition in a powdered free flowing form adapted to be dissolved in water prior to use for wood preservation comprising in admixture a member of the group consisting of arsenic pentoxide and alkali metal and ammonium arsenates which in 1.2% w./v. aqueous solution give a pH within the range of 2.0–3.6, a member of the group consisting of copper sulphate and zinc sulphate containing not more than 10% excess water, over theoretical $1H_2O$, and a member of the group consisting of potassium dichromate, ammonium dichromate and anhydrous sodium dichromate.

5. A wood preservative composition as claimed in claim 4 having a pH in 4% w./v. aqueous solution within the range of from 2.0–2.8.

6. A wood preservative composition as claimed in claim 4 having a pH in 4% w./v. aqueous solution within the range of from 2.1–2.25.

7. A wood preservative composition as claimed in claim 4 containing sodium bisulphate.

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