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FILLER COMPOSITION

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The present invention relates to improvements in a filler composition.

In the processes of finishing porous materials such as wood, it is sometimes necessary because of the fibrous character of the surface to lay a foundation for a finishing lacquer or varnish coat. This foundation serves to fill the pores of the wood which open upon the surface and thereby produces a smooth surface for the reception of the finishing coat. Without this foundation the finishing coat would tend to follow the contour of the surface of the wood resulting in an uneven coating falling into the depressions in the surface of the wood. A further difficulty in coating unfilled wood is that an excessive amount of coating material is required. It is known that an ultimately satisfactory coating can be prepared by repeated application of coatings and rubbing down the inequalities. However, this is impracticable from an economic standpoint since the most expensive part of the finish is the hand work required.

The art of wood finishing has, therefore, adopted the practice of filling wood, such as walnut, mahogany and others, before applying a finishing coating. For the purpose of accomplishing this filling, it is customary to apply as the actual filling material some inert substance such as silica or the like. A dry filling material, however, cannot be applied readily and furthermore will not remain in the pores of the wood during subsequent handling before the coating is applied. It is, therefore, recognized as necessary to provide some sort of binding agent along with the inert filling material. The most satisfactory binding agent prior to the present invention has been a drying oil. A filler of the oil type then comprises inert filling material, drying oil, hydrocarbon solvents, and usually a drying accelerator. Saponifying agents are sometimes used to react with part of the oil and thus increase the speed of drying. Such a filler can be applied, for instance, by brushing or spraying, and then remains open or workable for a period of some time depending on the rate of drying of the oil. In furniture finishing, for example, a filling operation may consist in having one man apply the filling composition by means of a brush or the like and pass the work to a second man who proceeds to pad the filler into the wood. This padding is accomplished by hand rubbing with a coarse cloth, tow or the like. With a handful of cloth or tow already soaked with partly dried filler, the filler is rubbed across the grain starting at the point where the composition was first applied by the

first workman. The operation is continued using a fresh handful of cloth or tow with a circular rubbing action all over the surface of the wood. In some cases, another rubbing with the grain is employed to remove most of the remaining excess filler. By means of this padding the filler composition is forced into the pores of the wood and any excess is sheared off at the surface. The filling operation may then be completed by a "ragging off" step which consists in going over the surface with a rag to remove fragments of tow or filler and to wipe any corners or carvings which would be missed by the padding. The ease and efficiency of the filling operation depend largely upon the physical properties of the filler. The filler must remain workable for a sufficient period of time to enable the complete working of the article. In the case of large pieces of furniture, for instance, this working period occupies a considerable period. In commercial production the time between application of filler and the first aftercoating is variable and the quality of the resulting finish is subject to correspondingly undesirable variation unless the filler remains workable throughout a substantial period. The action of the material in forming a pad on the rubbing cloth or tow is also important in securing uniform filling since once a good pad is formed, further rubbing gives a substantially uniform filling action on the whole surface being padded. The filler should also cut or rub off smoothly at the surface without pulling up out of the grain.

The oil fillers of the prior art have had quite satisfactory working properties in the respects just discussed. There are, however, several disadvantages to oil fillers which are well-recognized. One of the principal objections is that the drying depends upon a chemical action, namely, the oxidation of the oil. As a result of this, it is necessary to allow a substantial interval between the application and working of the filler and the application of the coating material.

A further disadvantage of the oil type filler is that it is not stable in contact with lacquers or varnishes. Pyroxylin lacquers are incompatible with the oil and the lacquer and filler mutually attack one another resulting in a failure of the coating. Any oil soluble stain used in the filler tends to bleed into whatever coat is applied thereover.

A still further disadvantage with an oil filler is that it is necessary, if a staining operation is to be combined with the filler, to use oil soluble stains. The oil soluble stains are generally unsatisfactory and fugitive and the staining opera-

tion is not generally satisfactory when done in this manner.

Instead of an oil filler, it has been proposed from time to time to use a water filler in which some water soluble or water dispersible binding agent is employed. The advantages of such fillers are numerous. No cheaper or more readily available solvent is known. The materials generally require only elimination of solvent in order to set. The highly superior water soluble wood stains can be used with them. However, water soluble or water dispersible fillers are not widely employed at the present time.

Among the commonly proposed binders of this class might be mentioned animal and vegetable glues, starches, gums, sugars, molasses, silicic acid, emulsions of waxes and resins, and mixtures of these materials with each other and with a wide variety of other substances. One objection to most of these materials is that they are organic in nature and subject to decomposition through fermentation, molding, etc. Another and very serious objection is that they require such high percentages of water for practicable application as to weaken their binding power to a dangerous degree. Coincidental with this high water percentage requirement is the fact that application of fillers containing such large amounts of water produces excessive grain raising.

Proposals to substitute various other materials as binders in water fillers have not been successful from a commercial viewpoint because the fillers proposed, among other things, were more expensive than oil fillers, more difficult to use, were not stable in storage, or required some particular treatment to prepare for use or to set them up after use.

It is an object of the present invention to provide an improved water soluble filler.

Another object of the invention is to provide a water soluble filler employing a novel water soluble resinous binder.

A further object of the invention is to provide an oil-free filler which sets by elimination of the solvent, permits the use of water soluble wood stains, and does not raise wood grain excessively.

A still further object is to provide a water soluble filler in which is incorporated a water soluble stain.

The above and other objects will become apparent from the following description and examples of the preferred form of my invention which is not, however, limited thereto but is limited only by the scope of the claims appended hereto.

I have found that a greatly improved water soluble filler can be prepared by the use of a resinous binding agent comprising a boric acid resin of a polyhydric alcohol, which resin is water soluble and retains its resinous properties upon drying out of water solution. Examples of the resins which I can use are the boric acid resins of the hexitols, glycerol, or ethylene glycol, among which the neutral resins of sorbitol and mannitol are preferred.

The hexitol borates for use in the present invention can be prepared as described in the applications of Clarence Bremer, Ser. Nos. 149,839, filed June 23, 1937; 196,387 and 196,414, both filed March 17, 1938; and 200,127, filed April 5, 1938. Unneutralized boric acid-hexitol resins are strongly acidic and for some applications this acidity may be objectionable. Moreover, the neutralized resins are more resistant to hydrolysis than the acidic resins. I, therefore, prefer

to neutralize the resin by the addition of an alkali hydroxide, preferably sodium or potassium hydroxide.

Instead of using a pure hexitol for preparing the resin a more economical commercial mixture can be employed. For example, in the case of sorbitol there is available a commercial syrup produced by the electrolytic reduction of glucose and which contains a major portion of sorbitol and also considerable quantities of non-hexitol polyhydroxy bodies. This material has been found to make resins with boric acid which are eminently suitable for the purpose of the present invention.

The filling agent used in the filler of the present invention may be any of the well-known inert materials used with the fillers of the prior art. As examples of such fillers may be cited the various forms of silica (such as quartz or siliceous), gypsum, slate-flour, diatomaceous earths, various pigments, and many others which will be apparent to those skilled in this art. Of particular value for general application is a transparent and finely divided inert such as siliceous. The diatomaceous earths are not generally suitable as the only filler because they are too light and fluffy. However, the bulking power of this filler is very useful when added to other harder inerts. Diatomaceous earths also assist in rubbing off the excess filler, keeping the filler workable longer, and imparting the property of rolling up when it is being rubbed off.

The preferred form of my filler also contains a surface active agent for the purpose of lowering surface tension. Lowering the surface tension increases the amount of surface spreading of the material and at the same time reduces the penetration of water into the wood by lowering capillary force which depends upon surface tension. A large number of surface active agents is known at the present time and among them may be mentioned sodium oleate, soaps, particularly soft soaps (not necessarily potassium soaps), partial fatty acid esters of inner ethers derivable from hexitols, for example, mannitan monolaurate or sorbitol monolaurate, these last two being particularly valuable in their commercial form such as those prepared by using mixed coconut oil fatty acids instead of pure lauric acid. The surface active agents mentioned are in no way exclusive but any of the usual surface active agents which do not adversely affect the resin or the aftercoating can be used.

In certain cases a filler containing water as the only solvent is found to dry too rapidly, that is, it does not remain open or workable for a sufficient period to enable the completion of the rubbing operation. In such a case a water soluble solvent can be advantageously included in place of part of the water. Suitable solvents for this are glycol and its water-soluble derivatives such as the cellosolves and the carbitols. These materials are solvents for the resins and are water miscible but have slower rates of evaporation than water, and so keep the filler open for a longer period. A further advantage to the use of these solvents is that they cause less grain raising than water. This is particularly important under circumstances in which the filler is used at great dilutions. If water alone were used it is possible in some cases that undesirable grain raising would result. This effect can be prevented by substituting a suitable portion of the non-aqueous solvents mentioned for part of the water.

It is frequently desired to include a stain with a filler and in such cases there are available for use in my filler a wide variety of water soluble stains. For example, Nigrosine 12525, Buffalo Black NBR, Croceine Scarlet M00, Wool Orange A, or Fast Wool Yellow 3GL can be used. These colors are intended merely to be suggestive to those skilled in the art and it is to be understood that this list is not by any means complete.

While the invention is capable of great variation as to proportions, the selection of fillers, stains, surface active agents and the like, the following examples will indicate to those skilled in this art some of the operative embodiments.

Example 1

A neutral sorbitol-boric acid resin useful in the present invention can be made as follows:

182 g. (1 mol) sorbitol and 62 g. (1 mol) boric acid dissolved in 180 g. of water were heated at 110–115° C. until the water of solution and 2 mols of water of condensation had been volatilized. The melt was then cooled to a temperature below 100° C. and a 50% aqueous solution of NaOH added until a pH of 7.0 was obtained. This neutralization required exactly 0.8 mol NaOH. Thereupon the neutralized mix was heated above 100° C. for sufficient time to evaporate the water introduced in the neutralization.

The product was an extremely viscous water soluble resin which had excellent binding power and which retained its resinous character upon drying out of water solution.

In the preceding example mannitol or any of the other hexitols can be substituted for sorbitol. In place of pure sorbitol, a commercial product containing a substantial quantity of sorbitol together with other polyhydroxy bodies can be used.

Example 2

A filler according to the invention can be prepared with the following composition, parts being by weight:

Silex	60
Sodium sorbitol borate (product of Ex. 1)	10
Water	5
Sodium oleate	1

The sodium oleate is suspended in the mixed borate and water. The silex is added and the whole mixed thoroughly in a suitable mill. The resulting composition is a powder which may be cut with water to any desired consistency for application. Color may be controlled by the addition of a water soluble stain.

Example 3

A filler which is colored by means of a mineral pigment in place of a stain can have the following composition, parts being by weight:

Silex	48
Burnt umber	12
Sodium sorbitol borate	10
Water	5
Sodium oleate	1

This composition is suitable for filling walnut. The mixture is prepared as in Example 2. Walnut filled with this mixture may be sanded lightly and coated with lacquer or varnish without the use of further stain or sealer.

Example 4

The compositions of Examples 2 and 3 contain water alone as solvent and are, therefore, rela-

tively quick-drying which makes them unsuitable for use on large pieces of wood in which the application and padding time exceed the drying time of the filler. The working life of the filler may be prolonged by the incorporation of ethylene glycol to slow the drying. A suitable composition can have the following proportions, parts being by weight:

Silex	48
Burnt umber	12
Sodium sorbitol borate	10
Water	2
Ethylene glycol	4
Sodium oleate	1

The composition is prepared similarly to that of Example 2, the ethylene glycol being incorporated in the liquid phase of the mixture.

Example 5

In place of sodium oleate which is the surface active agent of Examples 2 to 4 other agents can be used. A commercial surface active agent comprising principally a partial higher fatty acid ester of an inner ether derivable from a hexitol, for example, sorbide monolaurate of commercial grade, can be used. The physical character of the filler can also be modified by replacing part of the flinty silex by a bulky diatomaceous earth such as kieselguhr. A formula embodying these two modifications can have the following composition, parts being by weight:

Silex	32
Kieselguhr	16
Burnt umber	12
Sodium sorbitol borate	12
Water	2.4
Ethylene glycol	4
Monolaurate of sorbide (commercial)	0.4

Example 6

A glyceryl borate resin can be prepared as follows:

Heat 184 g. (2 mols) glycerol and 124 g. (2 mols) boric acid slowly, holding it at approximately 10 degree intervals until rapid boiling ceases at each temperature. Samples taken at different temperatures were very soft on cooling until the reacting mass reached 135° C. when the samples began to show signs of resin formation by thickening on cooling. At 145° C. the mass is becoming resinous. Cool to 100° C. and neutralize by the addition of 25 ml. of an aqueous NaOH solution of 500 g. per liter concentration. Reheat to 135° C. until rapid boiling ceases. The product on cooling is a fairly hard glassy resin.

In place of glycerol the same reaction can be performed by substituting ethylene glycol in the same molar ratio and heating until the mass becomes resinous. The product of such a reaction is a glycol borate resin.

Example 7

In place of a hexitol borate a satisfactory filler can be made with a glyceryl borate resin such as that of Example 6. A suitable formula can have the following proportions, parts being by weight:

Silex	52
Kieselguhr	8
Glyceryl borate	12
Sodium oleate	1
Water enough to form a creamy paste.	

This binder was then applied to a sanded oak panel. The filling was essentially satisfactory.

Example 8

A further modification in the resinous part of the filler is to substitute glycol borate such as that of Example 6 for the other resins. Such a composition can contain the following, parts being by weight:

Silex -----	52
Glycol borate -----	13
Sodium oleate -----	1
Water enough to form a creamy paste.	
Kieselguhr -----	8

A panel was filled successfully with this composition although it does not dry to as hard a film as the fillers prepared with hexitol resins.

The fillers of the present invention can be substituted directly for the oil fillers customary in this art. The same mode of application and padding can be used. Similar inert fillers are available. As distinguished, however, from the oil fillers, the fillers of the present invention can be coated at once when the water or other solvent has evaporated. There is no chemical change involved in the setting of this filler, but it is a simple drying out. The aqueous solvent is partly absorbed into the wood and partly evaporates. The small amount of water absorbed into the wood does not produce any undesirable effects in ordinary usage. Where a large quantity of solvent must be used and an all water solvent might produce grain raising, part or all of the water is replaced by glycol or a derivative thereof. The filler does not react adversely to a lacquer or varnish coating and there is no hydrocarbon solvent to eliminate. In the case of the ethylene glycol and its derivatives, the vapors are unobjectionable and do not injure an after coating if some residual portion is present.

In tests it was found that panels filled with the composition of the present invention and subsequently finished with lacquer held the finish out of the grain better than similar panels filled with oil fillers.

A further test showed that a panel filled with a commercial oil filler and finished with lacquer blistered badly when subjected to a temperature of 90° C. for 1 hour in an oven, whereas a similar panel finished with the same lacquer over a sorbitol borate filler of the type described herein retained its original finish under the same conditions.

Another advantage possessed by the fillers of the present invention is that wood filled with them can be sanded if desired. Such sanding can be performed as soon as the filler dries. In many finishing operations, particularly in fine finishing work, this is a real advantage, whereas it is recognized that an oil filler does not sand well due to rapid clogging of sand paper.

The invention is not to be taken as limited to the examples since other polyhydric alcohol boric acid resins which are water soluble and retain their resinous properties upon drying out of water solution can be used. Similarly, the other ingredients of the filler and the proportions thereof are subject to variation as already described. The consistency of the filler can be varied by controlling the amount of water (and water soluble organic solvent) used. For some purposes a relatively thick paste-like consistency will be preferred but for other purposes a brushable or even a sprayable consistency may be desired. In any case the consistency wanted can be obtained by using more or less liquid in the composition as will be apparent to those skilled in the art.

What is claimed is:

1. A filler comprising inert filling material and an aqueous solution of a water-soluble boric acid-polyhydric alcohol resin, said resin retaining its resinous character on drying out of water solution and being a binder for said filling material.

2. A filler comprising inert filling material and an aqueous solution of a water-soluble resin of boric acid and a polyhydric alcohol selected from the group consisting of hexitols, glycerol and ethylene glycol, said resin retaining its resinous properties upon drying out of water solution and being a binder for said filling material.

3. A filler comprising inert filling material and an aqueous solution of a water-soluble boric acid-hexitol resin, said resin retaining its resinous properties upon drying out of water solution and being a binder for said filling material.

4. A filler comprising inert filling material and an aqueous solution of a water-soluble boric acid-mannitol resin, said resin retaining its resinous properties upon drying out of water solution and being a binder for said filling material.

5. A filler comprising inert filling material and an aqueous solution of a water-soluble alkali metal neutralized boric acid-mannitol resin, said resin retaining its resinous properties upon drying out of water solution and being a binder for said filling material.

6. A filler comprising inert filling material, an aqueous solution of a water-soluble alkali metal neutralized boric acid-mannitol resin, said resin retaining its resinous properties upon drying out of water solution and being a binder for said filling material, and a surface active agent.

7. A filler comprising inert filling material and an aqueous solution of a water-soluble boric acid-sorbitol resin, said resin retaining its resinous properties upon drying out of water solution and being a binder for said filling material.

8. A filler comprising inert filling material and an aqueous solution of a water-soluble alkali metal neutralized boric acid-sorbitol resin, said resin retaining its resinous properties upon drying out of water solution and being a binder for said filling material.

9. A filler comprising inert filling material and an aqueous solution of sodium sorbitol monoborate, said monoborate being a binder for said filling material.

10. A filler comprising inert filling material, an aqueous solution of sodium sorbitol monoborate, said monoborate being a binder for said filling material, and a surface active agent.

11. A filler comprising inert filling material, an aqueous solution of a water-soluble boric acid-polyhydric alcohol resin, said resin retaining its resinous properties upon drying out of water solution and being a binder for said filling material, and an auxiliary solvent for said resin selected from the group consisting of ethylene glycol and water soluble derivatives of ethylene glycol.

12. A filler comprising inert filling material, an aqueous solution of a binder consisting of a resin of boric acid and a polyhydric alcohol selected from the group consisting of hexitols, glycerol, and ethylene glycol, said resin being water soluble and retaining its resinous properties upon drying out of water solution, and an auxiliary solvent for said resin selected from the group consisting of ethylene glycol and water soluble derivatives of ethylene glycol.

13. A filler comprising inert filling material, an aqueous solution of a binder consisting of a resin of boric acid and a polyhydric alcohol selected

from the group consisting of hexitols, glycerol and ethylene glycol, said resin being water soluble and retaining its resinous properties upon drying out of water solution, and an auxiliary solvent for said resin selected from the group consisting of ethylene glycol and water soluble derivatives of ethylene glycol, and a surface active agent.

14. A filler comprising inert filling material and an aqueous solution of a boric-acid resin of a polyhydric alcohol with not more than 6 hydroxyl groups, said resin being water soluble and retaining its resinous character on drying out of water solution and acting as a binder for said filling material.

15. A filler comprising inert filling material and an aqueous solution of a boric-acid polyhydric-alcohol resin, said resin being water soluble and retaining its resinous character on drying out of water solution and being a binder for said filling material, and a surface active agent.

16. A composition for dilution with water to produce a filler which comprises inert filling material and a boric acid-polyhydric alcohol resin as a binder for said filling material, said resin being one which will dissolve in added water and which retains its resinous character on drying out of water solution.

17. A composition for dilution with water to

produce a filler which comprises inert filling material and a boric acid-hexitol resin as a binder for said filling material, said resin being one which will dissolve in added water and which retains its resinous properties upon drying out of water solution.

18. A composition for dilution with water to produce a filler which comprises inert filling material and an alkali metal neutralized boric acid-mannitol resin as a binder, said resin being one which will dissolve in added water and retain its resinous properties upon drying out of water solution.

19. A composition for dilution with water to produce a filler which comprises inert filling material and an alkali metal neutralized boric acid-sorbitol resin as a binder, said resin being one which will dissolve in added water and retain its resinous properties upon drying out of water solution.

20. A composition for dilution with water to produce a filler which comprises inert filling material and a boric acid resin of a polyhydric alcohol with not more than 6 hydroxyl groups, said resin being one which will dissolve in added water and retain its resinous character on drying out of water solution and acting as a binder for said filling material.

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