

# PATENT SPECIFICATION

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## (54) IMPREGNATING LIQUID FOR WOOD AND WOOD PRODUCTS

(71) We, GORIVAERK AS, a Danish company of Birkemosevej 1, DK-6000 Kolding, Denmark, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to an impregnating liquid for wood and wood products and of the type containing a fungicidally active organo-tin compound and a binder dissolved in an organic solvent. Said liquid is particularly suitable for vacuum impregnation, but may also be used in other forms of impregnation, such as immersion or application.

A very widespread fungicide, also for use in wood impregnating liquids, is bis-(tributyl tin)oxide (TBTO), cf. for example British patent No. 1,059,629 and No. 1,419,373, Danish published application No. 133,336 and German published specification 2420235. The use of TBTO, however, as also emphasized in published application No. 133,336, involves certain disadvantages, for instance the unpleasant smell of the compound which is caused by its high vapor pressure, and its low washing- and UV-stability and resultant occasionally insufficient effectivity.

It has also been found that certain persons are allergic to the substance so that there occurs contact allergy phenomena which may cause skin irritations, just as the substance may cause headaches after using it for a shorter or longer period of time.

One or more binders also enter into current impregnating compositions on a solvent base, such as vacuum impregnation compositions, and these binders have, in principle, three functions:

(1) Fixation of the biocide so that the leaching is reduced or eliminated.

2) Improved adhesion of the compositions applied during subsequent treatment, in other words a primer effect.

3) Reduction of the water vapor permeability by stopping up the pores. In this way the surface is also rendered water repellent and the wood is dimension-stabilized against future moisture action.

Two different types of binder may be used, viz. the oxidative drying and the non-oxidative drying binders.

Oxidative drying binders used are, among others, for example low molecular alkyds, partly polymerized esters of glycerol or pentaerythritol and unsaturated carboxylic acids, such as tall oil fatty acids, as well as cyclopentadiene adducts to various oils.

The non-oxidative drying binders are for instance various polymers, such as so-called petroleum resin which is a polydiene resin, cumarone-indene resins, ketone resins, such as polycyclohexanone resins which may possibly be phenol-modified, as well as aldehyde resins, such as aromatic formaldehyde resins.

Impregnating liquids on the basis of TBTO usually contain major or minor amounts of oxidative drying binder. This may reduce the drawbacks involved in using TBTO, but unfortunately also reduces the fungicidal activity of TBTO, especially when used in high concentrations to fulfil the above-mentioned objects. The reduction at high concentrations is particularly due to an encapsulation of the TBTO molecules which is significant already at binder concentrations of about

7.5%. The additional drawback is added that the storing stability when using oxidative drying binder is low where the oxygen of air may have unimpeded admission to the liquid for long periods of time, which is the case for instance in vacuum impregnation plants. Said disadvantage can be reduced but not entirely eliminated by continual dosing of anti-oxidants to the liquid in the stockpile.

It has also been attempted to combine TBTO with non-oxidative drying binders. Normally, these do not noticeably reduce the fungicidal activity, but on the other hand they do not reduce the drawbacks involved in using TBTO either. On the contrary, it has been found in practice that they add a further disadvantage, causing in some cases poorer adhesion of the compositions subsequently applied, in other words a reduce primer effect. These drawbacks are so decisive that in practice TBTO is predominantly used in combination with oxidative drying binders.

The present invention is based on the surprising discovery that by reacting TBTO with a fatty acid a product can be obtained which has a similar fungicidal activity as TBTO but is much less irritant and more convenient to use. In addition the reaction products of TBTO with fatty acids can give products exhibiting excellent compatibility with non-oxidative drying binders in compositions suitable for use in impregnating liquids for wood or wood products especially by vacuum impregnation and can enhance adhesion of subsequently applied paints.

The present invention accordingly provides an impregnating liquid for wood and wood products comprising an organic solvent, as a fungicidally active compound a reaction product of tributyl tin oxide and one or more naphthenic acids, and as a non-oxidative drying binder a polydiene resin which is a polymerization product of an unsaturated  $C_8$  fraction from steam cracking of naphtha having an average molecular weight of about 1500. Typically the organic solvent is white spirit.

Such impregnating liquids are well-suited for vacuum impregnation of wood having extremely good storing stability, good penetration, and affording an effective and durable protection, as it is very stable against washing and ultraviolet light, and providing surprisingly good adhesion of the subsequently applied surface treatment systems.

The binder resins used in the invention continue satisfactory solubility and stability properties with a reasonable price. Such polydiene resins are sold for instance under the trade Marks "Escorez 1102B" and "Imprez 100".

An impregnating liquid according to the invention for vacuum impregnation of wood may suitably contain from 1/2 to 5 percent by weight of reaction product between TBTO and naphthenoic acid and from 2 to 20 percent by weight of the non-oxidative drying binder dissolved in an organic solvent, such as white spirit, said combination providing the most balanced penetration and dimension stability.

A particularly suitable combination is 2 percent by weight of tributyl tin naphthenate and 5 percent by weight of polydiene resin, said combinatin providing by normal impregnating practice a satisfactory protective effect in accordance with the existing regulations.

Other protectants may also be added, such as UV-absorbing agents, particularly hydrophobically active surfactants, anti-surface mould agents, penetration-promoting agents and dyes.

These various protectants may be used to supplement the fungicidal activity of TBTN so as to obtain the most suitable spectrum of protection in consideration of the expected loadings of the impregnated product, but as a principal rule there is not obtained a protection surpassing that which might be expected from the properties of the agents concerned.

It has surprisingly been found, however, that a particular anti-surface mould agent, viz. 2,4,5,6-tetrachlorisophthalonitrile, displays a synergy action with the constituent fungicide, represented by TBTN, the obtained wood protection surpassing by far the expected additive effect of the individual componets, as documented below.

By means of the compositions according to the invention the disadvantages known from TBTO are completely eliminated:

The reaction product used according to the invention, in the following named TBTN, is almost odourless, and no case of headaches has been reported as a result of using the composition.

The skin-irritating effect of the composition has also been examined in TBTO-sensitive persons, and it does not exceed the effect of a blind test with white spirit.

The fungicidal activity has been examined by means of the so-called sobeto

test where wooden blocks were impregnated with the test compound and put into the soil for 5 weeks were exposed to a test fungus (*Coniophora cerebella*) with and without intermediate washing treatment, respectively. Thereafter the percentage weight loss was determined, untreated blocks being used as control.

The results will appear from the below table where reaction products of 50% TBTO and 50% naphthenic acid, reacted at 120°C, were used as active substance.

TBTN, calculated as % TBTO	Intermediate Washing	Weight Loss %	
		Treated	Untreated
0.6	+	0.04	25
0.6	-	0.56	28
0.8	+	0.29	26
0.8	-	0.58	25
1.0	+	0	23
1.0	-	0.52	18
1.2	+	0.89	27
1.2	-	1.8	26

The compositions used were as follows:

TBTO	0.6%	0.8%	1%	1.2%
Reaction product	1.2%	1.6%	2.0%	2.4%
Polydiene resin	9.5%	12.0%	15.0%	18.0%
Solvent (white spirit)	89.8%	86.4%	83.0%	79.6%

In this standard test the maximum weight loss permissible is 3%, and it will thus be seen that the examined concentrations are all satisfactory.

By way of comparison it is stated that the lower limit at which unreacted TBTO gives a satisfactory result in this test is 0.75%, which shows that improved fungicidal activity is achieved by using TBTN.

Finally, experiments have been made as to the influence of the various impregnating compositions on the adhesion of various paint systems on an oil base, alkyd base, acryl base, and polyurethane base, respectively, on planed pinewood panels of the dimensions 200 × 100 × 16 mm.

The panels were immersed in the impregnating liquid for 1—2 minutes and 24 hours after the impregnation 4 different paint systems were applied in 2 layers at 24 hours' interval between application of the individual layers.

The degree of adhesion was determined according to Swedish Industrial Standard (SIS) 184 171 "tensile test" with tensile test specimen of an area of 3,14 cm<sup>2</sup> to which had been glued a solvent-free two-component epoxy adhesive. The results stated below are mean values of the 4 different paint systems, for each of which 3 tensile test determinations were made.

Tensile Force  
per unit Area

1.1% of TBTO + 7.2% of oxidative drying binder

2.82 MPa

1.25% of TBTO + 7.5% of non-oxidative  
drying binder (polydiene resin)

3.05 MPa

1.0% of TBTO as 2% of TBTN + 7.5% of  
non-oxidative drying binder

3.17 MPa

It will hence be seen that the best adhesion is achieved by the combination of TBTN and non-oxidative drying binder. Even in case of longer drying times and after a 1-year weathering test (outdoor exposure with test panels facing towards the south inclined at an angle of 45° to the vertical) this combination is judged to be fully up to the standard of TBTO in combination with oxidative drying binder as regards primer effect.

#### *Fungicidal Activity in Soil Contact*

The fungicidal activity in soil contact has been examined by the so-called Mullåda test (Nordic Wood Preservation Committee, standard (NWPC) 1412/70 "Testing against surface rot". In this test 2 x 10 x 70 mm beech sticks, impregnated with the test composition in a quantity of 150 kg/m<sup>3</sup> were placed in soil for 6 weeks. Untreated control sticks were used in comparison, and tests were carried through with and without an intermediate washing treatment. The weight loss at the end of the test period is a measure of the efficiency of the compositions.

It is pointed out that this test simulates very hard conditions for vacuum impregnated wood, as it is normally advised not to use such wood in direct soil contact precisely on account of the risk of decomposition owing to surface rot and surface mould. Still, it is of course an advantage that the wood exhibits the best possible resistancy in this test, and this also indicates an even exceptionally good resistancy when used out of soil contact.

In the present case an examination has been made partly of an impregnating liquid according to the invention containing 2 percent by weight of TBTN in combination with 5% of a non-oxidative drying binder ("Escorez 1102 B"), partly, in comparison, an impregnating liquid containing only 1 1/2% of 2,4,5,6-tetrachlorisophthalonitrile in combination with "Escorez 1102 B", and finally of an impregnating liquid according to the invention containing 1.8% of TBTN and 0.2% of tetrachlorisophthalonitrile (TCIPN).

The following results were obtained:

Active Substance	Intermediate Washing	Weight Loss %	
		Treated	Untreated
2% of TBTN + 5% of Escorez	+	10.5	18.5
—, —	—	10.2	18.6
1.5% of tetrachlorisophthalonitrile + 5% of Escorez	+	8.6	16.2
—, —	—	9.6	15.3
1.8% of TBTN + 0.2% of TCIPN + 5% of Escorez	+	1.4	14.6
—, —	—	0.2	14.1

It will be seen that the composition according to the invention containing a combination of TBTN and tetrachlorisophthalonitrile shows a surprisingly low weight loss compared to the weight loss when using the individual constituents. Tests with larger amounts of nitrile have produced no significantly improved effect.

#### WHAT WE CLAIM IS:—

1. An impregnating liquid for wood and wood products comprising an organic solvent, as a fungicidally active compound a reaction product of tributyl tin oxide and one or more naphthenic acids, and as a non-oxidative drying binder a polydiene resin which is a polymerization product of an unsaturated C<sub>5</sub> fraction from steam cracking of naphtha having an average molecular weight of about 1500.

2. A liquid as claimed in claim 1 containing from 1/2 to 5 percent by weight of the tributyl tin oxide carboxylic acid reaction product and from 2 to 20 percent by weight of the binder.

3. A liquid as claimed in claim 2, containing 2 percent by weight of tributyl tin naphthenate and 5 percent by weight of polydiene resin.

4. A liquid as claimed in any one of claims 1 to 3 and containing an anti-surface mould agent.

5. A liquid as claimed in claim 4 wherein the agent is 2,4,5,6-tetrachlorisophthalonitrile.

5 6. A liquid as claimed in claim 6, containing about 0.2 percent by weight of 2,4,5,6-tetrachlorisophthalonitrile. 5

7. A liquid as claimed in any one of claims 1 to 6 and substantially as hereinbefore described.

10 8. Wood or a wood product treated using the liquid claimed in any one of claims 1 to 7. 10

9. A method of treating wood or a wood product which comprises impregnating the wood or wood product with a liquid as claimed in any one of claims 1 to 7.

15 10. A method as claimed in claim 9 and substantially as hereinbefore described. 15

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