Chipboards as raw material of furniture

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Abstract. The problem of using wood materials in residential premises is closely related to the issues of forestry. This is due to the fact that the wood subsequently processed into materials and products emits a gas harmful to humans – formaldehyde. In Russia, there are strict requirements for the permissible level of formaldehyde in the air (0.01 mg/m³) both in residential premises and in the atmosphere. The environmentally friendly wood emits formaldehyde. The emission of formaldehyde may exceed the permissible level up to 10 times when obtaining chipboards using urea-formaldehyde and phenol-formaldehyde resins. Such an excess of the permissible level of formaldehyde is especially characteristic for chipboards. Moreover, a much larger amount of formaldehyde is emitted from urea-formaldehyde and phenol-formaldehyde resins during their hot curing than it is in the liquid resin in its free form. Therefore, much attention in this work is paid to the curing process of urea-formaldehyde and phenol-formaldehyde resins in relation to the manufacturing conditions of chipboards. The study of this process was based on the models related to the manufacturing conditions of chipboards using the microscopy method. It was found that some formaldehyde is preserved in vapor-gas bubbles and eventually moves out the chipboards.

1. Introduction
The volume of chipboard production both in the world and in Russia is constantly growing. In Russia, in 2019, the annual output was 9986 thousand m³. Despite the growth of board production, the problem of its toxicity still remains relevant. To meet the requirements of formaldehyde permissible level (PL), the artificial boards can be used in residential premises only if they have the limited saturation of the air volume in the room. Moreover, in real conditions of using the cabinet furniture made of chipboards in residential premises, the board saturation of the air volume is much higher than PL requires.

A distinctive feature of this work from the previous ones is that it includes theoretical calculations of the chipboard permissible saturation of the air volume in residential premises based on the emission class of the produced boards, the Russian and foreign indexes of formaldehyde PL, which allows us to imagine the problem of reducing the toxicity of boards; microtechnological studies of the process of resin hardening in chipboard, which made it possible to understand the mechanism of formaldehyde "freezing" in the adhesive film. We also studied the efficiency of chemical preparations in the particleboard technology, which have not only the property of a formaldehyde scavenger, but also a wood preservative and hardener of urea-formaldehyde resins (UFR). The most effective products were patented.

When analyzing the existing formaldehyde PL, we proceeded from the following. Due to the high toxicity of chipboard produced by the domestic industry and, in this regard, with the current problem
of using chipboard to make furniture, JSC VNIIDrev and ANO TsSL Lessertika raised the question: can domestic furniture manufacturers make products that emit no more than 0.01 mg/m³ of formaldehyde? Their data show that even laminated particleboards and plywood emit 2-7 times more formaldehyde than PL.

According to A D Platonov, Yu S Mikhailova [1,2] the wood releases more formaldehyde than PL requires. Their studies on the concentration of formaldehyde in the oak and beech wood show that the maximum formaldehyde concentration (about 0.35 mg/m³ of air) is when the wood humidity is close to fresh wood. When the wood moisture content decreases to 7-8%, a monotonous decrease occurs and the formaldehyde concentration is less than 0.1 mg/m³. Therefore, there is a question of growing such wood so that when drying and using it in furniture structures, there should be no release of formaldehyde, which is one of the problems of forestry.

For comparison, it should be noted that a similar foreign standard for the release of formaldehyde from wood-based panels is 10-12 times higher than the Russian one and it is 0.1 ppm or 0.124 mg/m³ in Western Europe and 0.11 mg/m³ – in North America. The Association of Furniture Industry Enterprises has repeatedly appealed to the Customs Committee to amend the regulation by harmonizing it with the relevant international standards. Despite this the standard of PL in Russia still remains at the same level.

At the same time, in foreign practice a higher standard (0.124 mg/m³ of air) has been adopted as a safe level of formaldehyde for humans, in contrast to the standard in our country (0.01 mg/m³ of air). Based on a number of studies [3-7], the Institute for Risk Assessment (Germany) has developed a document ("Conclusion of the Federal Institute for Risk Assessment of March 30, 2006") on the toxicological assessment of formaldehyde and its "safe" level for humans, in which it concluded that the permissible concentration of formaldehyde in the air, called the "safe" level for humans is 0.1 ppm (parts per million) or 0.124 mg/m³ of air [8].

From the results of studies [8] on the short-term effects of formaldehyde on humans, the Institute established the minimum levels of detection of formaldehyde: from mild to moderate eye irritation - from 1.0 ppm (1.24 mg/m³ of air) and higher; irritation of the nose (throat) – from 2.0 ppm (2.48 mg/m³ of air) and higher. Based on the results of a number of studies on long-term exposure to formaldehyde on humans (an average of 10 years), the Institute established a minimum level of detection of the harmful effects of formaldehyde, equal to 0.2-0.3 ppm (0.248-0.372 mg/m³ of air).

Based on the results of studies of a number of its works, the institute established the NOAEL level (the maximum dose at which there is no detectable harmful effect), equal to 0.1 ppm. This level was adopted as the "safe" concentration of formaldehyde for humans.

This level coincides with the level of the World Health Organization (WHO), which, as a justification for the value of this level, indicates that "only a very small part of the population reacts with any irritation to the formaldehyde action at a concentration of 0.1 ppm."

When analyzing the reasons for the "preserving" of formaldehyde in chipboards, we proceeded from the need to conduct microtechnological studies in relation to board technology [9-11].

The purpose of this work is to analyze the existing PL of formaldehyde; the toxicity of artificial boards; to prove the low board saturation of the indoor air volume to meet the requirements of PL; to study the resin hardening process to explain the "freezing" process of formaldehyde in finished boards and to find the effective formaldehyde scavengers to reduce the toxicity of boards.

The key problem for the chipboard industry is the revision of the existing PL of formaldehyde in the air and the reduction of formaldehyde emission from the boards using effective methods, one of which is the use of complex action chemicals in the technology. Therefore, the main direction of our work in solving the problem of reducing the emission of formaldehyde from chipboard was finding such effective products which would also be good wood preservative and resin hardeners with their subsequent introduction into practice.

2. Materials and methods
The low board saturation of the indoor air volume was proved theoretically meeting the requirements
of PL. We used a mathematical model developed earlier (given below) that connects the maximum permissible chipboard saturation of the indoor air volume with a number of parameters.

A mathematical model – IS = [(Sat \cdot PEL_{tox}) \cdot PEL_{E1}] 
\cdot S \cdot h, \text{ m}^2/\text{room}; IS – the irreducible board saturation of the room volume, \text{m}^2 of chipboards/room; Sat – the board saturation of air by the chamber method, \text{m}^2/\text{m}^3 of air; PEL_{tox} – the permissible exposure level of F in the air of residential premises (0.01 mg/m^3 of air) according to the standards, mg/m^3 of air; PEL_{E1} – the permissible exposure level of F from the boards of the certain classes of F emission, mg/m^3 of air; V – the room volume, \text{m}^3; S – the area of the room, \text{m}^2; h – the ceiling height, m.

The analysis of the reasons for formaldehyde "preserving" in chipboards using UFR and phenol-formaldehyde resins (FFR) as a binder was carried out as follows: Models of adhesive films were made from UF and PFR. These models passed the stage of heat treatment as applied to the particleboard technology at temperatures from 100 to 170 °C. After that, microscopic studies of the films were carried out using a Carl Zeis Jena scanning electron microscope. The magnification of the films was from 50 to 5000 times.

To study the efficiency of formaldehyde binding by acceptors, chipboards with a thickness of 16 mm, and a density of 750 kg/m^3 were produced using UFR of the UF-O brand, the content of which (by dry matter to the mass of absolutely dry chips) was 13% for the outer layers of the plates and 10% for the inner layer. Ammonium chloride was used as the hardener in the calculation of 1-2% by weight of the liquid resin with a concentration of 60%. Wood species used for the chips was a mixture of birch, aspen and pine. Hot pressing of the plates was as follows: the temperature was 170 °C; pressure – 2.4 MPa; duration – 0.35 min/mm of board thickness (5.6 min excluding auxiliary operations). The following chemical preparations were used in the experiments: sodium pentachlorophenolate (SPCP) that according to our data turns into pentachlorphenol during the chemical reaction in the chipboards, sodium silicofluoride (SSF), and KhMBB-3324, which included sodium dichromate, copper sulfate, sodium tetraborate, and boric acid in a mass ratio of 3:3:2:4, respectively. The content of preparations (by dry matter) in the board ranged from 1 to 2% by weight of absolutely dry chips. SPCP was introduced into the resin, followed by its dissolution in the latter. Since SPCP is alkaline, the content of ammonium chloride in the resin was 2%. SSF was also introduced into the resin, which did not contain ammonium chloride, since SSF itself has the property of a resin hardener. KhMBB-3324 was applied to the chips in the form of an aqueous solution, followed by drying the chips to 3%. The release of formaldehyde from the plates was determined by perforator and chamber methods.

Thus, the purpose of these studies was to: analyze the existing formaldehyde PL and the toxicity of wood and chipboards; prove a low board saturation of the indoor air volume to meet the requirements of the PL; study the resin curing process to explain the process of formaldehyde preservation in the finished boards; find the effective formaldehyde scavengers to reduce the toxicity of artificial boards.

3. Results and discussion

The proof of the low board saturation of the indoor air volume to meet the requirements of PL is shown in the graphs of figures 1-5, which are obtained by the calculation using the developed mathematical model as shown in method section. The following designations are accepted in these graphs: \( H_{max}, \text{ m}^2/\text{room} \) – the maximum permissible board saturation of the indoor air volume (for example, the indexes are for a room of 20 square meters with a ceiling height of 2.5 m); PEL – the permissible exposure limit of formaldehyde (or PL) in the air of residential premises according to both the domestic and foreign standards; E1 and E2 – formaldehyde emission classes according to GOST 10632-2014 [12]; H – the board saturation of the test chamber volume when testing them for the release of formaldehyde by the chamber method, \text{m}^2/\text{room}.

In the calculations of formaldehyde PEL, the domestic standards of 0.01 mg/m^3 of air (as well as the foreign standards (0.124 mg/m^3 of air), are adopted; which is proved by a number of foreign studies [13]).

Calculations were made for 2 groups of furniture provided for by GOST 30255-2014 [14];
1) cabinet furniture, tables, beds of panelled construction;
2) furniture for sitting and lying, beds with soft backs and elements.

When testing the chipboards by the chamber method used for various groups of furniture, GOST 30255-2014 established its own board saturation of the test chamber volume (in the graphs, the index of \( H, \text{m}^2/\text{m}^3 \) on the X-axis). For the boards of the 1st group such saturation should range from 0.95 to 1.05 m\(^2\) chipboard/m\(^3\) of chamber air, and for the boards of the 2nd group, it should range from 0.285 to 0.315 m\(^2\) chipboard/m\(^3\).

Comparing graphs 1-3 for the 1st group of boards, the maximum board saturation of the room with a 20 m\(^2\) surface ranges from 3.84 to 81 m\(^2\), depending on the indexes of \( H, \text{PEL} \) and formaldehyde emission class. Figures 1-2 show that the index of \( H_{\text{max}} \) is very low for boards according to domestic standards for the formaldehyde release. Depending on the formaldehyde emission class, it ranges from 3.84 m\(^2\) (for Class E1) to 6.56 m\(^2\) (for Class E0.5). This means that in a room of 20 m\(^2\), you can install furniture only with this total area and only then the concentration of formaldehyde in the indoor air will be at the level of PEL. But these indexes of the boards’ area in the room do not correspond to the real conditions for installing the cabinet furniture made of chipboards both in the offices and residential premises. Figure 3 shows that if PEL is 0.124 m\(^2\)/m\(^3\) of air in such a room, you can install furniture made of larger boards – from 48 to 81 m\(^2\).

Figures 4 and 5 show the same indexes for the 2nd group of furniture. When PEL is 0.01 m\(^2\)/m\(^3\), the \( H_{\text{max}} \) index ranges from 1.2 to 2.0 m\(^2\)/m\(^3\), depending on the formaldehyde emission class. When PEL is 0.124 m\(^2\)/m\(^3\), the \( H_{\text{max}} \) index is much higher and ranges from 14 to 25 m\(^2\)/m\(^3\), depending on the formaldehyde emission class.

![Figure 1](image1.png)

**Figure 1.** The dependence of the maximum board saturation of the indoor air volume for the 1st group at PEL of formaldehyde of 0.01 mg/m\(^3\) in the air and the formaldehyde emission class of boards E0.5.

![Figure 2](image2.png)

**Figure 2.** The dependence of the maximum board saturation of the indoor air volume for the 1st group at PEL of formaldehyde of 0.01 mg/m\(^3\) in the air and the formaldehyde emission class of boards E1.
Figure 3. The dependence of the maximum board saturation of the indoor air volume for the 1st group at PEL of formaldehyde of 0.124 mg/m³ in the air and the formaldehyde emission class of boards E0.5 (the upper curve) and E1 (the lower curve).

Figure 4. The dependence of the maximum board saturation of the indoor air volume for the 2nd group at PEL of formaldehyde of 0.01 mg/m³ in the air and the formaldehyde emission class of boards E0.5 (the upper curve) and E1 (the lower curve).

Figure 5. The dependence of the maximum board saturation of the indoor air volume for the 2nd group at PEL of formaldehyde of 0.124 mg/m³ in the air and the formaldehyde emission class of boards E0.5 (the upper curve) and E1 (the lower curve).
Thus, for the boards of the 1st group, the index of $H_{\text{max}}$ is very low for the boards according to the domestic standards of formaldehyde release. Depending on the formaldehyde emission class, it ranges from 3.84 (for Class E1) to 6.56 m$^2$ (for Class E0.5). For this group of boards and foreign standards of PEL, you can install furniture made of larger boards in a room of 20 m$^2$– from 48 to 81 m$^2$. The same is true for the boards of the 2nd group. When PEL is 0.01 m$^2$/m$^3$, the $H_{\text{max}}$ index ranges from 1.2 to 2.0 m$^2$/room, depending on the formaldehyde emission class. When PEL is 0.124 m$^2$/m$^3$, the $H_{\text{max}}$ index is much larger and ranges from 14 to 25 m$^2$/room, depending on the formaldehyde emission class.

The micrographs in figure 6 show the types of adhesive films, the curing of resins (UFR and FFR) in which took place at room temperature (23 °C and at a temperature of 100-170 °C. Figures 6 and 7 show the micrographs of the curing process of UF-O (with 1% of ammonium chloride) and SFZh-3014 (one-component, without hardener) resins. It can be seen from the micrograph in figure 6 that during the curing of the binder, even in the cold state (figure 6a, UFR), microvoids (bubbles) were formed in the binder mass. When exposed to temperature, the voids increase in size (figure 6b, UFR), especially when the temperature changes from 105-110 to 140-150 °C. This indicates that the cured mass of the binder located on the periphery of the voids and in its other parts still has mobility under the influence of a higher temperature on it (105-110 °C). This process differs in many respects from the process of phase structure formation during the flow of melts of polymer mixtures, as well as the influence of relaxation phenomena on the physical properties of polymer materials. This distinctive feature is typical of UF and PFR, in contrast to nanostructured composites [14]. Heat treatment of a binder containing a significant amount of a hardener (1% by weight of resin) for 10 min does not lead to the completion of the oligomer polycondensation reaction, the molecules of which still have a mobile state. At the first stages of polycondensation, the hardened mass of the binder, which is a shell of voids (vapor-gas bubbles), is, as it were, in a separate state. The shells of these bubbles hardly touch each other. At deeper stages of curing, the shells of neighboring bubbles come closer together and, ultimately, they seem to coalesce, forming a spatial structural-mechanical lattice, which is especially clearly seen in figure 7c – FFR. There is a great analogy with UFR curing when we see the hardening process of FFR.

During the curing of these binders, voids are formed in the cured mass (figure 7a, FFR). Under the influence of intragas pressure, the bubble increases in size and its contours change (figure 7b, FFR).
The hardened mass of a binder is distributed in the adhesive layer in the form of areas of various configurations. In contrast to the process of UFS curing, during the FFR curing, even at 140-150 °C for 10 min, such a large crust (shell) of the cured mass does not form on the periphery of the adhesive layer as during UFR curing (figure 6c, UFR). During the solidification of the mass, the vapor-gas mixture has time to escape through the cracks in the bubbles. Even if such a shell is formed (figure 6c, UFR), it is only at a high temperature (170 °C). At the same time, the strength of its individual sections is not so high as to prevent the vapor-gas mixture from leaving the adhesive layer. In the micrographs, the peripheral part of the hardened mass of both UFR (figure 6d, UFR) and FFS (figure 7d, FFR) has breaks of greater or lesser size. When exiting, the mixture breaks the shell of such a bubble and makes peculiar channels in the solidified mass. This causes cracks in the hardened mass (figure 6d, UFR and figure 6d, FFR). Cracks in the curing mass of the binder appear, apparently, due to the shrinkage of the binder during its curing. Ultimately, the areas of the cured mass of the binder at a temperature of 110-170 °C have significant destruction, which increases with increasing temperature and the duration of treatment of the specimens at this temperature. The obtained micrographs explain the reason for the low strength of the cured binder mass.

Unlike the previous opinion about the solidity of the cured binder mass in the chipboards, in fact, this mass is in a porous, crumbling state.

**Figure 7.** Micrographs of the edge zone of FFR hardened at temperature, °C (with magnification, times): (a) 110 (80); (b) 130 (250); (c) 150 (170); (d) 170 (3000).

The micrographs in figure 7 show that part of formaldehyde, being in the composition of the vapor-gas mixture, remains in the cured adhesive layer. Over time, formaldehyde is filtered through the destroyed shells of vapor-gas bubbles and escapes outside. As our research has shown, this type of adhesive layer in chipboard poses the danger of additional release of formaldehyde from the finished boards during their deformations associated with transportation and cutting. It is rather difficult to quantify the amount of formaldehyde released. If earlier it was believed that a thin layer of hardened binder mass (15-30 μm thick) has a monolithic structure, the results of the work showed that this is far from the case, as it can be seen from micrographs. It turns out that the cured adhesive layer between the wood particles is not monolithic at all, but is saturated with voids ("bubbles"), in which the vapor-gas mixture was preserved together with formaldehyde.

The search for effective formaldehyde acceptors was carried out in the direction of the search for
products with a complex action. As a result, such products have been found: sodium pentachlorophenolate (SPCP); sodium fluorosilicate (SFS) and KhMBB-3324. The novelty of this research lies in the fact that these products have double, and some of them even triple action. All of them have the property of an effective antiseptic and are successfully used for bioprotection of wood. In addition, with the same efficiency they can be used for bioprotection of chipboards. So, SFS preparation additionally has the property of a hardener of urea-formaldehyde resins. The results of experimental-industrial testing have shown the effectiveness of their use in reducing toxicity and bioprotection of boards. The resulting boards met the requirements of the current GOST 10632 for the emission of formaldehyde of E0.5-E1 classes.

The formaldehyde PL in the air, equal to 0.01 mg/m³, is practically unfeasible for board manufacturers, as well as furniture producers in particular. The hardened binder is a porous mass within which the steam-gas mixture is concentrated together with formaldehyde. When the boards are deformed, the intensity of formaldehyde released from them can increase due to the formation of additional cracks in the adhesive layer. Three preparations of complex action (SPCP, SFS and KhMBB-3324), recommended for practical use in the particleboard technology, have shown their effectiveness in the action of both formaldehyde acceptors and antiseptic and UFR hardener. Their use in practice will make it possible to produce plates mainly of the E1 formaldehyde emission class.

4. Conclusion
1. The current permissible level of formaldehyde in the air, equal to 0.01 mg/m³, is very low, which creates a big problem not only for board manufacturers, but also for consumers, mainly furniture producers.
2. The adhesive film between wood particles in chipboard is a porous structure consisting of a large number of voids (bubbles) inside which a vapor-gas mixture is “frozen” together with formaldehyde. Over time, formaldehyde is released from the boards. When the boards are deformed, the intensity of formaldehyde released from them can increase due to the formation of additional cracks in the adhesive layer.
3. Three complex-acting products (SPCP, SFS and KhMBB-3324), which significantly reduce the release of formaldehyde and ensure their biosecurity, have been recommended for practical use in the chipboard technology. In addition, SFS replaces the use of ammonium chloride, which contains chlorine harmful to humans, for curing urea-formaldehyde resins in chipboard.

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