Phosphonic acid as a component of low flammability particle boards

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Abstract. The possibility of using dibasic hydroxyethylidene diphosphonic acid to reduce the flammability of particle boards has been considered. A formulation was compiled with the addition of amino alcohols, surfactants and other auxiliary compounds, conventionally called the fire retardant Palonot. Wood substrate (veneer) was impregnated with various amounts of Palonot, and the development of combustion during ignition and subsequent attenuation with a regular increase in heat loss to the environment was studied. The results were compared with amidophosphate, which has found industrial use in fire protection of wood-based materials. The manufactured three-layer boards withstood the test in the "fire tube" and met the main requirements of the current standards for general-purpose boards. The thermomechanical curves and the details of the process of adhesion of the binder to the substrate containing the flame retardant are provided. The conditions for the manufacture of wood-based materials with the patented Palonot have been analyzed.

1. Introduction
Phosphonic acids are dibasic acids of the general formula RP(O)(OH)₂. Their anhydrides are good phosphorylating agents. Phosphonic acid derivatives are of great practical importance as pesticides, surfactants, drugs, etc.

We were interested in the opportunity to expand the range of phosphorus-containing compounds that can be used in the production of wood-based panels and together with which new opportunities will open up in the modification of low-combustibility particle boards (LCPB). As a rule, for fire protection, developers use salts of tribasic phosphoric acid, phosphates [1-4]. Amidophosphate grade KM has found application in industrial production [5, 6]. Phosphonates have not found proper use even in research due to a large price difference between chemical compounds and boards. However, the a priori accepted opinion may turn out to be wrong. The advantages can be revealed in the technology, properties, and in the process of operation of the LCSB. Because of this, we tested the possibility of using phosphonic acid as a component of LCPB using the developments of the Finnish company Palonot Oy which created and patented the fire retardant Palonot [7].

2. Materials and Methods
The optimal composition of Palonot contains hydroxyethylidene diphosphonic acid (HEDP, the trivial name is etidronic acid), 49.2%; monoethanolamine, 10%; ammonia water, 20.6%; surfactant, 3.6%; and additional water 16.6%. The recipe can vary within wide limits, the "working" component is HEDP acid (1):
The proportion of phosphorus in the acid is 30.1%. The composition is obtained by mixing the components, preferably at a temperature from 10 to 60 °C with an optimal pH value from 5 to 6.5. The composition is supplied in the form of a solution or gel.

Amidophosphate KM is synthesized according to the method described above [5, 6], pH 4.5, concentration 50%.

As a wood substrate, 1.5 mm thick peeled birch veneer was used. The binder used was melamine-carbamide-formaldehyde resin (MKFS, STO 00203789-057-2012). Ammonium chloride and ammonium sulfate were used as hardeners.

Birch veneer was impregnated with fire retardants with a variable level of treatment, conditioned and tested by the semicircle method according to BS [8] and DIN [9]; the length of the combustion front advance until attenuation (L, mm) and the time of advance along the sample sections (the entire length of the 800 mm sample was broken into 12 equal sections) were recorded. Indicators used: flame propagation speed (v, mm / s), attenuation angle (A, deg), and flame propagation resistance index (M). The M index was determined according to BS and DIN by the formula:

\[ M = \frac{1.04 \cdot \tau^*}{L^{5/2}}, \]

where, \( \tau^* \) is the duration of self-burning, s.

Thermomechanical curves and performance of adhesion were determined according to well-known methods described, for example, in the book [10].

The chipboard was manufactured on a pilot plant of the university by applying a fire retardant solution to wood particles, the chips were dried to a moisture content of 1.8%, treated with an MKFS solution, a carpet of 400 x 400 mm was formed and pressed in a press of the AKE Mariannelund brand at a temperature of 200 ± 2 °C in the mode of 0.3 min / mm of the finished board thickness.

3. Results and Discussion
The results of testing samples with different mass fractions of two fire retardants by the semicircle method are shown in figure 1 selectively for different content of absolutely dry fire retardants. The full characteristics of the parameters of all tested options are presented in table 1.

Under equal conditions of veneer impregnation due to different properties of the prepared fire retardant solutions (viscosity, polarity), the levels of processing did not strictly coincide. Interpolation makes it possible to correctly compare the effectiveness of the studied fire retardants. It was not possible to resort to the standards of the Russian Federation, since large-size samples of boards of pilot production are required for testing, and tests can be carried out in specialized organizations.
Figure 1. The rate of flame propagation in samples treated with Palonot (1, 3) and KM (2) with a mass fraction: 1 - 2.68%; 2 - 3.08%; 3 - 4.83%.

The complex nature of the curves in the figure is due to ambiguous combustion conditions. At the initial moment of ignition, the course of the curves is determined by the ignition source (burner flame) 50 mm high. The flame covers a slightly larger distance of the sample to self-combustion, which reaches a maximum on the curves. Then, under the influence of increasing heat losses due to heat transfer outside the sample by changing the angle of inclination of combustion in a semicircle, combustion is suppressed with subsequent attenuation. Note that the angle of the sample position on the semicircle varies from +90 degrees through 0, and further to –90 (if the sample does not decay earlier, as in the case of control).

Table 1. The effectiveness of the two fire retardants as measured by the semicircle test.

| Fire retardant brand | Processing level, % | Maximum speed, mm/s | Time to reach it, s | Parameters |
|----------------------|---------------------|---------------------|-------------------|------------|
|                      |                     |                     |                   | L, mm      |
|                      |                     |                     |                   | A, degrees |
|                      |                     |                     |                   | M          |
| Palonot              | 2.68                | 8.4                 | 72.1              | 517        |
|                      |                     |                     |                   | –26.71     |
|                      |                     |                     |                   | 49.47      |
| Palonot              | 4.83                | 5.0                 | 72.2              | 477        |
|                      |                     |                     |                   | –17.71     |
|                      |                     |                     |                   | 54.24      |
| Palonot              | 6.38                | 5.9                 | 71.2              | 478        |
|                      |                     |                     |                   | –18.10     |
|                      |                     |                     |                   | 47.19      |
| KM                   | 3.08                | 6.6                 | 68.6              | 470        |
|                      |                     |                     |                   | –16.21     |
|                      |                     |                     |                   | 56.08      |
| KM                   | 5.72                | 4.7                 | 78.2              | 412        |
|                      |                     |                     |                   | –2.99      |
|                      |                     |                     |                   | 63.33      |
| KM                   | 7.47                | 4.4                 | 82.4              | 405        |
|                      |                     |                     |                   | –1.43      |
|                      |                     |                     |                   | 62.53      |

These tables allow us to normalize the indicators by interpolation to the same content of both fire retardants to compare their inhibitory ability. Controls are not included in the table. They are very different from the tested samples and it makes no sense to compare them. The maximum burning rate is almost three times higher. The samples burn out completely over the entire length of 800 mm, the angle –90 degrees taken into account as the attenuation angle is not determined, since there is no attenuation and the sample completely burns out in the candle-like mode.
The time parameters of the combustion of samples with the considered fire retardants indirectly indicate some difference in the manifestation of the attenuation mechanism. The time to reach the maximum speed during ignition depends in different ways on the content of the fire retardants. This seems natural if we take into account the multicomponent composition of Palonot, the components of which have their own specific combustion, in particular, monoethanolamine and surfactants.

Thus, the reduced level of substrate treatment, corresponding to the content of fire retardants, counting on dry matter, allows us to consider the suppressed combustion process in slow stages and reveal their effect on the combustion process, and not just give the answer: when ignited, the sample itself burns or does not burn. The latter would take place with a higher content of fire retardant.

According to the semicircle method, Palonot exhibits good fire-retardant properties, but it does not show any clear advantages of phosphonates over phosphates. Moreover, in terms of combustibility, Palonot samples (within the limits of the study) are somewhat inferior in inhibition of combustion to amidophosphate KM: the combustible length in comparable values increases by 13%, and the attenuation angle is 40% greater than in the samples containing KM. An increase in the parameters L and A characterizes an increase in heat loss during the passage of the combustion front in a semicircle and a decrease, as a result, of the return heat flow to support self-combustion. These difficulties are smaller in the presence of Palonot than KM. The M index also appears to be about five units lower. Of course, other fire test methods can give a different estimate of the effectiveness of the phosphonate, but it is clear that testing based on self-sustaining combustion and suppressing it with a low consumption of flame retardant did not produce an encouraging result.

Therefore, it is advisable to consider other aspects due to which the use of Palonot can be justified. It turned out that the presence of amino groups in monoethanolamine should have a plasticizing effect on the wood complex, thereby opening up the possibility of reducing the specific pressure. This is interesting when organizing the production of LCPB at outdated factories and “weak” presses. By the method of taking thermomechanical curves (figure 2) we found that Palonot actually plasticizes the particleboard. The first temperature transition in the chips containing Palonot is recorded at 74 °C, and in the control chips a little later, at 86 °C. The difference in favor of Palonot is more evident in the high temperature range, corresponding to the pressing of the panels.

![Figure 2. Thermomechanical curves of samples of wood particles treated with a fire retardant (1) and control (2).](image-url)
When taking TM curves after pressing the shavings into a plate, the difference with the control disappears. This indicates that the flame retardant has undergone transformations during hot pressing with a loss of plasticizing ability. In finished boards, such a property is not required; plasticization, if preserved, would reduce the elastic modulus.

The study of the effect of fire retardant treatment of wood particles on the change in adhesion ability upon contact with the working solution of the binder showed that the wetting of the substrate surface improves due to the fire retardant, and the performance of adhesion increases, in particular, from 0.112 to 0.291 J/m². An increase in the adhesion strength can be expected, although the overall strength of the LCPB is a function of a number of factors. Let’s discuss some of them.

The priority is given to the structure and spatial arrangement of wood particles in the carpet. Model consideration of the carpet [11] indicates that one cannot expect exclusively the variant of contacts of wood particles with the participation of a binder (i.e., gluing in the variant “particle - glue with glue - particle”). A certain proportion is made up of contacts according to the second option, i.e. with the application of binder on only one particle; the third option is simply contacts of the surface of wood particles with each other without a binder. The latter option determines the presence of hidden defects in a finished board. In addition, due to the brevity of hot pressing, in deformed particles relaxation is incomplete; therefore residual stresses contribute to a decrease in the overall strength of the chipboard.

In order to fit into the existing technology without introducing an additional stage of drying the wood-based pulp after treating it with aqueous solutions of fire retardants, we tested the method of introducing Palonot in the form of a gel. Taking into account the high concentration of fire retardant (73%), we calculated the possibility of eliminating additional drying by introducing the following changes: increasing the degree of drying of wood particles in the normal mode with partial use of the working solution feed points in the mixer, supplying a fire retardant through them instead of a binder. The second part of the flame retardant is introduced into the binder itself in a strictly admissible ratio and order due to the studied compatibility of the binder with the flame retardant.

Trial production of three-layer boards with a ratio of inner and outer layers of 50:50, with a consumption of melamine-carbamide-formaldehyde binder 10 and 12%, respectively, and with the introduction of Palonot exclusively into the outer layers at the rate of 21% or 10.5% if calculated for the entire board (all based on the dry weight of substances) showed that laboratory-made LCPB correspond to bending strength ($\sigma_{\text{ben}}$) and density 748 kg/m³ required by GOST 10632-2014 in general purpose boards. The data, compared with control (without flame retardant) samples, are presented in table 2.

| Samples                          | $\sigma_{\text{ben}}$, MPa | $E_{\text{el}}$, GPa |
|----------------------------------|---------------------------|---------------------|
| Flame retardant specimens        |                           |                     |
| containing Palonot in outer layers | 12.53                     | 1.39                |
| Control samples                  | 13.50                     | 1.50                |

The modulus of elasticity decreases slightly, the swelling index, on the contrary, improves, making up a fraction of 0.68 from the control. The samples withstand the fire tube test. In industrial conditions a greater uniformity of quality is achieved with an improvement in performance compared with those obtained in laboratory conditions.

4. Conclusions
1. Phosphonic acids can be used as a fire retardant for particle boards, for example, as a compound of Palonot. It is important to determine the technological advantages that will make the project commercially viable. A high concentration of the retardant in the form of a gel, if used correctly, will eliminate the additional (after the introduction of traditional fire retardants) stage of drying the mass. When introducing the technology in existing production facilities, the installation of additional...
equipment is critically important. If the problem is solved by recipe changes and auxiliary additions, the feasibility is determined by economic calculations and becomes more real.

2. Technical solutions aimed at the production of LCPB can be extended to the fire protection of other wood materials, the structure of which includes a wood substrate in one form or another and a binder such as amide-formaldehyde resins (MKFS, KFS), including medium density fibreboard, wood-laminated plastics, and plywood, subject to the modification features [10].

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