OPTIMIZING THE FORMULATION OF A FILM-COATING COMPOSITION, FORMING A NON-TRANSPARENT AND HARD-COMBUSTIBLE COVER ON WOOD*

Panayot A. Panayotov[1], Rumen Krastev[2], Violeta Y. Petkova-Ruseva[2]

[1]University of Forestry, 1756 Sofia, Kl. Ohridski Boulv. 10, Bulgaria

[2]Central Laboratory of Physico-Chemical Mechanics, BAS, 1113 Sofia,
Acad. G. Bonchev Str., Bl. 1, Bulgaria

1. INTRODUCTION

Wood is a combustible material and for this reason wooden structures need suitable fire protection. To this end, two methods are applied: deep impregnation with antipyrene solutions and surface protection with hard-combustible coatings, [9]. A combination of both methods is implemented for some more responsible objects. The application of surface protection is the more preferred method, since it is more easily realized [12]. Depending on the aesthetic outlook and function of the object, varnishes and paints are used for the formation of hard-combustible coatings. Varnishes are preferred as coatings on interior wainscoting and interior structures made of hard-combustible massive wood or hard-combustible wooden materials. They preserve the natural pattern of wood. Paints are usually placed on wooden roof structures. They are developed in two variants: paints forming non-swelling and swelling coatings [10; 12; 15]. The non-swelling coatings are placed on preliminarily impregnated wood or on hard-combustible wooden materials. The swelling coatings may be formed on non-impregnated wood too or on combustible wood materials in the amount ensuring the respective degree of fire protection, [10; 12; 15].

The present work considers the possibilities for obtaining an optimal composition of the Ognebar fire-protective paint, forming a non-transparent and hard-combustible coating on wood. The objective of this investigation is to determine the effect of the quantity of the components introduced in the fire-protective paints on the properties of the swelling coatings formed with them: adhesion, hardness and combustibility. These protective covers should possess high adhesion to wood and good operation parameters: retarded flame propagation and satisfactory hardness.

2. MATERIALS AND EXPERIMENTS

Spruce wood (Picea Abies Karst) was used to determine the adhesion of the polymer coatings to the wood substrate. To this end, test specimens were prepared with sizes 20x50x50 mm, the last dimension being along wood fiber direction. Thirty test specimens with radial structure were produced for each test series. The coatings were formed by a soft brush in 5 layers, each subsequent layer being placed after drying of the previous one. The method used for determining the adhesion is in conformity with the regulations of BDS EN 24624-2004, [4]. The method consists in vertical extortion of the coating from the bearing substrate by means of a metal cylinder (stamp) glued on the coating. The stamp is made of alloy or steel and has a diameter of 20 mm. It is glued on the coating by means of a contact cyanacrylate technical adhesive. The adhesion test was carried out 7 d after gluing the stamps. The destructive force was determined by applying a tensile force at such a rate that destruction would occur after 1 ± 0,5 min.

The adhesion (σ_a, N/mm^2) is determined according to the equation (1):

$$\sigma_a = 0{,}0032.F \qquad (1)$$

where: F is the destructive force, N.

The obtained experimental results for the adhesion were statistically processed [14].

The hardness of the coating characterizes the resistance of a solid body against the penetration in it of another solid body. Several methods for determining the hardness of coatings have found application in practice: with a pendulum, with a micro- hardness meter, and with a pencil. The hardness of the coatings was determined using the pendulum method (M-3) according to the regulations of BDS EN ISO 1522:2007, [2]. The hardness is determined as the ratio between the time for the pendulum attenuation on the coating and the time for the pendulum attenuation on a standard glass plate [2]. The samples with coating were formed with paint on glass plates with dimensions 50/100 mm and a thickness of 5 mm. The tests were made under room conditions at a temperature t = 23 ± 2 ºC and relative humidity φ = 50 ± 5 %. The hardness values were calculated in arbitrary units according to equation (2):

$$H = \frac{t_0}{t_k} \qquad (2)$$

where: t_o – time for attenuation of the pendulum oscillations on the test specimen, s;

t_k - time for attenuation of the pendulum oscillations on the standard glass plate, s.

The pendulum is deviated to the respective angle (6º for the pendulum of König) and is then released with the simultaneous turn-on of a chronometer or another time measuring device. The time for decreasing the amplitude from 6º to 3º (for the pendulum of König) is recorded (in seconds). The measurement is made at three different places on one and the same test specimen. Each single result and the average value of the three measurements are recorded. The thickness of the dry coating should be at least 250 μm.

The degree of combustibility of the film coatings is established according to the standard valid in Bulgaria BDS ISO 1210: 1997 (BDS 10457-1988), known as the “foil method” [1;5]. The criterion for the assessment of the coating combustibility according to this standard is the “length of flame propagation" parameter. Thin aluminum foil specimens with a thickness of 0.015 mm and dimensions of 100x230 mm are used in this method. The coating is formed only on one side of the foil by 5-time spreading with a flat brush after 24 h periods of drying. Five specimens are tested for each composition. The film coating is dried under room conditions (t = 22±3°C and φ = 65±5%) in the course of one week and is then treated in a drying oven for 6 h. After drying the specimens are cooled in an exiccator over calcium dichloride in the course of 2 h and then they are ready for testing. The flame treatment is realized in a heating chamber without air circulation. The specimens are placed in a vertical double frame, pressed with two clamps in the top part. The flame treatment is applied by means of a propane-butane torch with a diameter of 1 mm, situated at an angle of 45° with respect to the horizontal surface. The distance between the torch and the lower part of the specimen is 10 mm.

The torch is adjusted in such a manner that the flame length is 25 mm. The duration of flame treatment is 15 s. The criteria for the combustibility degree assessment are: the length (height) of the burnt or charred (carbonized) part of the coating, the duration of the independent burning after removing the impulse and all phenomena accompanying the burning. The length of the charred part should not exceed 200 mm, in order to classify the coatings as hard-combustible materials. The independent burning should not last more than 15 s and there is a requirement for the absence of burning drops. The method corresponds to BS476: Part 12:1997, for fire impulse of type "A" item 5.3.1; item 5.7 and DIN 53438.

Four components were used for the composition of a paint forming the hard-combustible non-swelling coating: binding substance, plasticizer, fire inhibitor and pigments. Alloprene R20 chlorinated rubber, a product of the ICI Company – England, was applied as a binder. Liquid chlorinated paraffin Chlorparaffin 48, a product of the HOECHST Company – Germany, characterized by 48 % of paraffin content, was used as a plasticizer. Diantimony trioxide Ab_2O_3 was used as a fire inhibitor. Titanium-white and zinc-white were applied as pigments in the ratio of 2:3 mass parts, rendering white color to the varnish base {zinc-whiting: zinc-white: zinc(II) oxide (zinc oxide: ZnO); titanium-white: titanium dioxide (titanium dioxide: TiO_2)}. The planned levels of component variation are presented in Table 1, [7; 8; 11; 13; 14]. The sum of the relative parts of the components for each planned composition is 100 %, [11; 13]. The planned 27 experimental combinations of the components are given in Table 2.

Table 1.Plan of the experiment

Components of the compositions	**Levels of variation**
Binding substance, x_1, %	15, 20, 25, 30, 35, 40, 50, 55
Plasticizer, x_2, %	5, 10, 15
Fire inhibitor, x_3, %	20, 25, 30, 35, 40
Pigments, x_4, %	10, 15, 20, 25, 30, 40

3. RESULTS

The mean arithmetic values of the obtained results for the planned 27 combinations are presented in Table 2 – columns 6, 7 and 8. It is seen that the adhesion values vary from 1.55 N/mm² to 5.55 N/mm². The relative hardness values are within the range from 0.25 to 0.40. The independent burning with a flame lasts from 1 s to 8 s after the impulse removal, i.e. all variants of the coatings are hard-combustible.

The obtained results were processed and analyzed using MS Excel. Theoretical polynomial models were composed, containing first and second degree terms of the components as well as their products [7; 13; 14]. The function of the LINEST multiple linear regression was applied for determining the regression coefficients of these models according to the least square method. The coefficients with a relatively high standard deviation were removed from the theoretical regression, simplifying it in this manner. The simplified models, obtained according to the above described procedure, are presented analytically (equations 3; 4 and 5) and graphically (Fig. 1; Fig. 2 and Fig. 3).

3.1. Theoretical model of adhesion

The theoretical model of the adhesion of the coating to wood, presented with equation (3), is obtained with determination coefficient $r^2 = 0.957$.

$$\sigma_a = 1.74 - 0.077 \cdot x_2 + 0.00122 \cdot x_1^2 + 0.000065 \cdot x_1 x_2 x_3 \text{ , N/mm}^2\text{,} \quad (3)$$

where x_1, x_2, x_3 are the relative shares of the respective components in %.

The content of the fourth component in the mix (the pigments) supplements the shares to 100 %.

Figure 1 shows the surface plot for the influence of the binding substance in the fire inhibitor on adhesion for plasticizer amount of 10 %.

Table 2. Experimental parameters of the investigated coatings

Compo-sition No	**Components of the compositions**				**Experimental parameters**		
	***x*1, %**	***x*2, %**	***x*3, %**	***x*4, %**	**σa, N/mm²**	***H*, arb. units**	**τ, s**
1	15	5	40	40	1.85	0.38	1
2	15	10	40	35	1.67	0.35	1
3	15	15	40	30	1.55	0.30	1
4	20	5	40	35	1.75	0.36	3
5	20	10	40	30	1.70	0.35	2
6	20	15	40	25	1.60	0.30	2
7	25	5	40	30	2.88	0.32	1
8	25	10	40	25	2.75	0.39	3
9	25	15	40	20	2.64	0.40	3
10	30	5	35	30	2.85	0.37	3
11	30	10	35	25	2.85	0.35	3
12	30	15	35	20	2.85	0.33	3
13	35	5	35	25	3.05	0.32	3
14	35	10	35	20	3.05	0.32	3
15	35	15	35	15	3.12	0.30	3
16	40	5	30	25	3.25	0.30	5
17	40	10	30	20	3.50	0.30	5
18	40	15	30	25	3.85	0.29	5
19	45	5	35	15	4.12	0.29	2
20	45	5	30	20	4.25	0.32	5
21	45	5	25	25	4.25	0.35	8
22	50	5	30	15	5.50	0.30	2
23	50	5	25	20	5.25	0.35	2
24	50	5	20	25	4.85	0.30	3
25	55	10	20	15	5.05	0.30	8
26	55	10	25	10	5.55	0.25	7
27	55	5	25	15	5.35	0.31	1

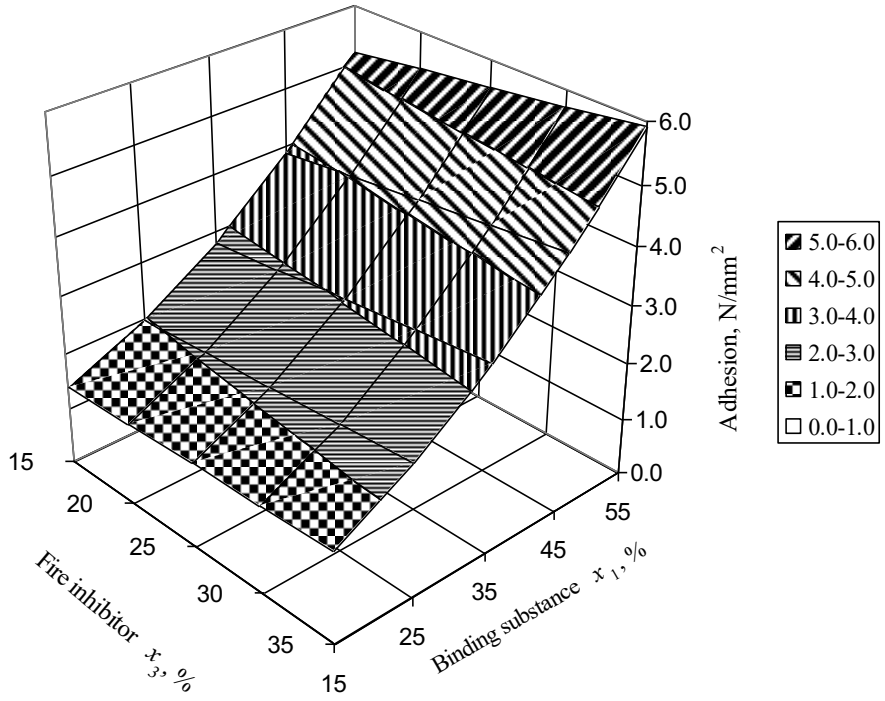


Fig. 1 Changes in the adhesion of the coating to spruce wood depending on the amount of the fire inhibitor (x_3) and binding substance (x_1) components

As seen in the figure (Fig. 1) and from the model (equation 3), the adhesion is substantially increased with the rise of the binding substance amount. The adhesion is slightly increased with the growth of the fire inhibitor amount. The analysis of the theoretical model of adhesion shows that the effect of the plasticizer on adhesion is negligible and that the increased pigment content reduces slightly the adhesion. The adhesion is 3.5 N/mm^2 for 40 % of binding substance, and it is 4.5 N/mm^2 for 50 % of binding substance.

3.2. Theoretical model of hardness

The theoretical model for the hardness of the coating, presented by equation (4) is obtained with a coefficient of determination $r^2 = 0.36$. Due to the high degree of data scattering it has been accepted not to use a more complicated theoretical model.

$$H = 0.23 - 0.0011 \cdot x_2 + 0.0018 \cdot x_3 + 0.0018 \cdot x_4 \qquad (4)$$

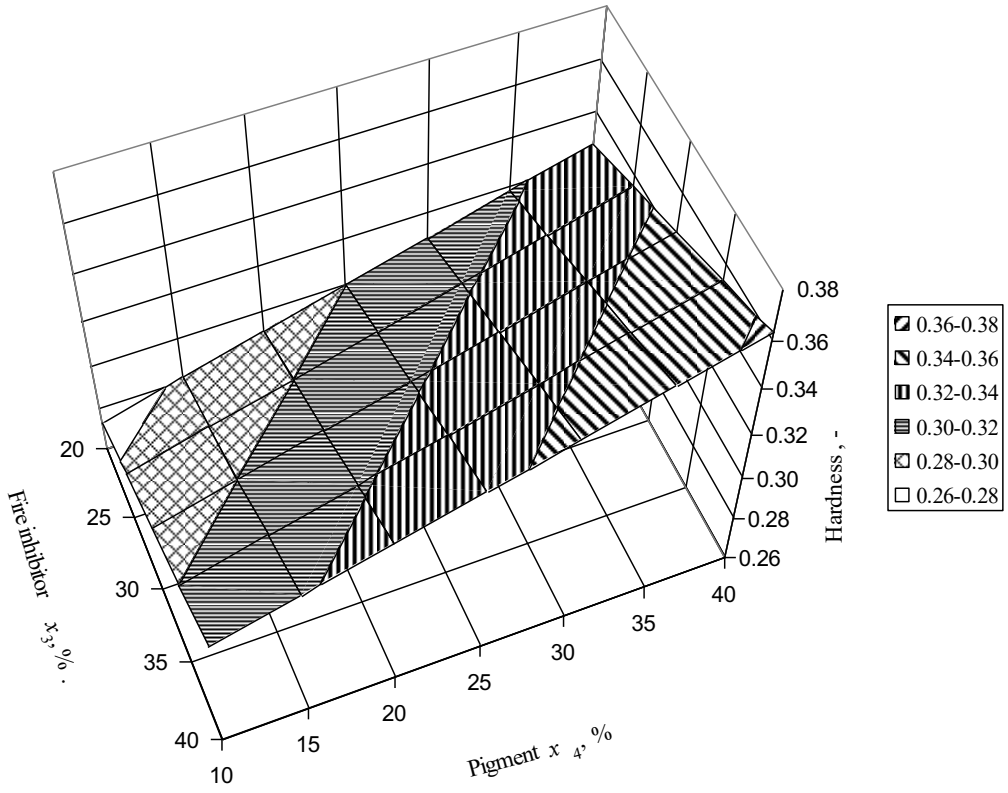


Fig. 2 Changes in the hardness depending on the amount of the fire inhibitor (x_3) and the pigment (x_4) components, for plasticizer amount of 10 %

It is established from the analysis of Fig. 2 and equation (4) that the hardness increases with the growth of the fire inhibitor and pigment quantities and slightly decreases with the growth of the plasticizer amount. According to the model, for 10 % of plasticizer, 10 % of fire inhibitor and 40 % of pigments, the coating exhibits hardness of 0.31 arbitrary units.

3.3. Theoretical model of combustibility

The theoretical model of the combustibility of the coating is described by equation (5), its coefficient of determination being 0.58. The model is graphically presented in Fig. 3, for plasticizer amount of 10 %.

$$\tau = -113.5 + 3.75 \cdot x_1 + 3.51 \cdot x_3 + 0.40 \cdot x_4 + 0.0270 \cdot x_1^2 - 0.0325 \cdot x_3^2 - 0.0498 \cdot x_1 x_3 - 0.0156 \cdot x_1 x_4 \quad (5)$$

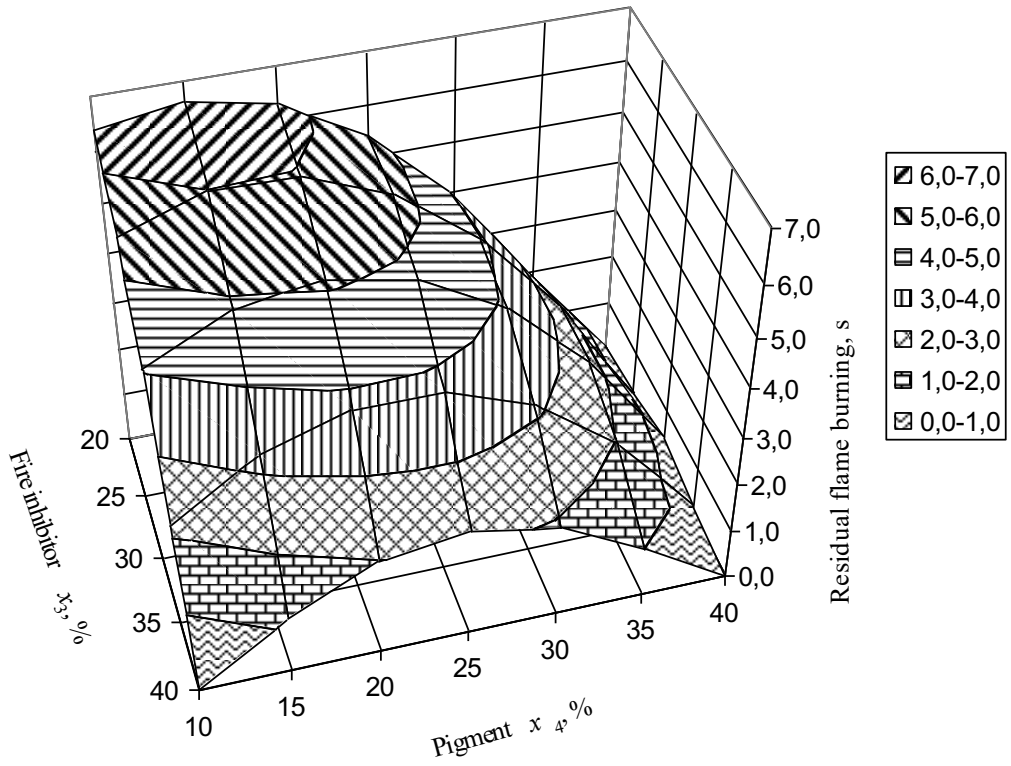


Fig. 3 Changes in the residual burning with a flame (τ) depending on the amount of the fire inhibitor (x_3) and pigment (x_4) components

The analysis of this model proves that with increasing the amount of pigments and fire inhibitor the independent burning with a flame decreases and almost vanishes. With increasing the amount of the binding substance the independent burning lasts longer. The shortest residual burning with a flame is observed for the compositions with 40 % of fire inhibitor and/or 40 % of pigments.

4. CONCLUSIONS

The obtained results provide the grounds for drawing the following conclusions:

1. The amount of the binding substance exerts the most significant effect on adhesion, which has satisfactory values for optimal binding substance content from 40 % to 60 % of the incorporated components.

2. With increasing the quantities of the fire inhibitor and the pigments, higher hardness values are observed.

3. The residual burning is significantly decreased with increasing the amount of the pigments and the fire inhibitor.

4. In accordance with the obtained results, the composition of the Ognebar paint, consisting of 40 % of binding substance, 10 % of plasticizer, 10 % of fire inhibitor and 40 % of pigments, may be accepted as optimal with respect to adhesion, hardness and residual combustibility.

The results of the mathematical models of the most important properties of the coating, obtained with the optimized composition of the Ognebar paint, provide the grounds to recommend its application in building practice for the formation of hard-combustible coatings on massive wood, impregnated with antipyrenes.

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