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Decreasing formaldehyde emission from medium density fiberboard panels produced by adding different amine compounds to urea formaldehyde resin

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ABSTRACT

In this study, medium density fiberboard panels were produced by adding different ratios of some amine compounds to urea formaldehyde resin, which had 1:1.17 mol ratios. The formaldehyde contents, physical, and mechanical properties of medium density fiberboard panels were determined according to EN standard methods.

In this study, it was determined that the formaldehyde emission emitted from medium density fiberboard panels decreased by adding urea, propylamine, methylamine, ethylamine, and cyclopentylamine solution. It was found that the water absorption and thickness swelling values increased slightly; however, the internal bond strength, modulus of rupture, and modulus of elasticity of medium density fiberboard panels also increased substantially, but these properties of medium density fiberboard panels decreased by adding higher ratios of urea solution. It was found that the formaldehyde emission of medium density fiberboard panels decreased 16.5% by using a 16% rate of urea formaldehyde resin and 0.8% rate of urea and ethylamine solution. These decreases were determined as 57% for cyclopentylamine solution addition, 41% for propylamine solution addition, and 48% for methylamine solution addition.

1. Introduction

Amino resins being used to bond composite wood products have an extremely important role in forest products, such as in medium density fiberboard (MDF), particleboard (PB), oriented strand board (OSB), and plywood (PW).

About 90% or more of the world's board production is made with urea formaldehyde (UF) resins [1]. UF resins, the most well-known amino resins, have many advantages such as low cost, ease of use under a wide variety of curing conditions, the fastest reaction time in hot press, water solubility, low cure temperatures, resistance to microorganisms and to abrasion, excellent thermal properties, and their colorless qualities, especially the cured resin compared to other resins. However, UF resins are not suitable to produce boards with good exterior exposure resistance. The biggest drawback of UF resins also is that they release formaldehyde into the environment during curing when they are used as a binder component [1–4].

Many products were produced with formaldehyde based resins, which emitted formaldehyde vapor and lead to consumer dissatisfaction and health related complaints. These emissions have caused various symptoms, the most common of which are irritation in the eyes and the upper respiratory tract [5–7]. When the human body is exposed to formaldehyde in high doses there is a risk of serious poisoning, and prolonged exposure can lead to chronic toxicity and even cancer [8,9]. For these reasons, regulatory pressure has recently reduced or eliminated formaldehyde emissions from wood products on a world-wide scale.

One of the common effective methods to decrease the formaldehyde content of resin is to change the mole ratio of formaldehyde to urea in UF resin. Several workers declared that the emission of formaldehyde from wood based panels lessened as the mole ratio decreases, the other physical and mechanical properties were adversely affected [10–13]. The other method has been the use of chemical additives called formaldehyde scavengers to reduce formaldehyde emitted from wood based panels. The most common scavengers are compounds containing primary or secondary amine such as urea, ammonia, melamine, and dicyandiamide [14]. It is known that urea is extensively used to decrease formaldehyde emitted from wood based panels bonded with thermosetting adhesive. Other formaldehyde scavengers such as tannin, resorcinol, peroxides, and ammonia treatment are expensive and not very effective. The addition of urea to resin does not cause problems in particleboard production. However, the formaldehyde scavengers must be carefully used, and they will adversely affect all properties of these panels [15–18].

On the other hand, Ebewele et al. [19,20] determined that the water resistance and flexibility of long-chain aliphatic primary diamines were improved by better glue line stress distribution in

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the cured UF resin network. For this reason, it is possible that using some amine compounds might enhance the mechanical and physical properties of MDF panels. The purpose of this study is to evaluate the applicability of urea (US), propylamine (PAS), methylamine (MAS), ethylamine (EAS), and cyclopentylamine (CPAS) compounds to reduce the levels of released formaldehyde from MDF panels bound with UF resin. The effects of these amine compounds on the mechanical and physical properties of these MDF panels were also investigated.

2. Materials and methods

2.1. Materials

Hardwood fibers of 85% and softwood fibers of 15% obtained from Çamsan A.Ş., Turkey were used in this study. These fibers were screened to remove bundles of fiber, and were then dried at 100 °C to obtain a 2–3% moisture content.

2.1.1. Bonding agent and other chemicals

In this study, the UF resin which had a 1:1.17 molar ratio of formaldehyde to urea was used. It also had a solid content of 65% (density: 1.237 g/cm^3, pH: 8.45, viscosity: 280 cps at 25 °C, flowing point at 25 °C). A 2% ammonium chloride (NH_4Cl) (solid content 20% dry resin basis) was added as a hardener for UF resin. A 2% wax solution (solid content 33% dry solid wood basis) was added to UF resin to develop the moisture resistance of the MDF panels. The chemicals used as formaldehyde scavenger in MDF production were urea, propylamine, methylamine, ethylamine, and cyclopentylamine. The control panels without amine solution were produced for each of the panels added with the used amine solution. The values of the control panels are shown in Figs. 1–6. The degrees of purity of all the used amine chemicals varied between 70% and 100%. All the used amine chemicals were prepared at 20% based on the weight of these chemicals. The degree of purity of the amines was taken into account when preparing the amine solutions.

The amount of UF resin (oven dry solid wood basis) and different amine solution ratios are presented in Table 1.

2.1.2. MDF panel manufacture

The wood fibers were placed in a rotary drum tank for uniform diffusion of UF resin. The UF resin and other chemicals were mixed and then applied by spraying into the tank. At the end of this process, fiber mats were produced in a hot press added pressure level system at 170 °C temperature. The MDF panels were prepared at 30 cm × 30 cm × 10 mm (length × width × thickness), and produced at a target density of 790 ± 10 kg/m^3. The MDF production was duplicated for each amine concentration. The press parameters belonging to the fiber mats produced are listed in Table 2.

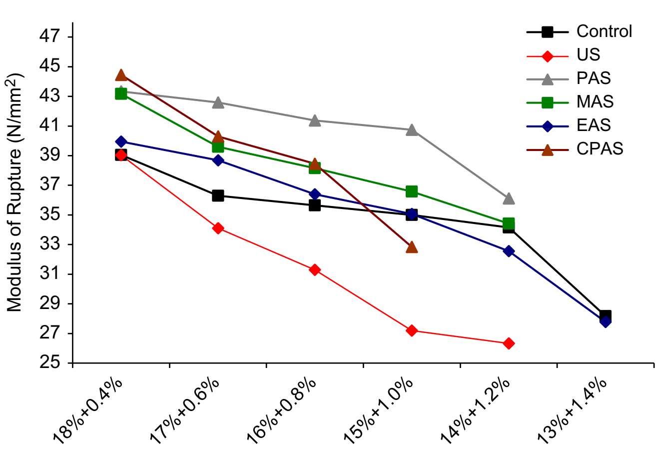

Fig. 1. Modulus of rupture (MOR) values of MDF panels.

Table 1
UF resin and different amine solution ratios used in the experimental parameters.

UF resin ratio (%)	18	17	16	15	14	13
Amine solution ratio (%)	0.4	0.6	0.8	1.0	1.2	1.4

Control panels were produced without amine solutions.

Table 2
Press parameters for MDF panels (temperature 170 °C).

	I step	II step	III step
Pressure (bar)	50	30	60
Time (s)	45	30	270

2.2. Methods

2.2.1. Mechanical and physical testing method

Four panels were produced for each amine concentration for the necessary experiments. All MDF panels were trimmed and sanded (0.3 cm on every surface) using sandpaper with a 150 grit size. The panels were pre-conditioned 65% relative humidity at 25 °C until they reached equilibrium moisture content before the mechanical and physical experiments. The mechanical properties, such as modulus of rupture (MOR), modulus of elasticity (MOE), and internal bond strength (IB) were determined in accordance with EN 310 [21] and EN 319 [22] standards. The physical properties, such as thickness swelling (TS) and water absorption (WA) were determined after 24 h soaking in water in accordance with EN 317 [23].

2.2.2. Formaldehyde emission by perforator method

For this study, the perforator test of MDF panels was determined after 14 days. The German Regulations for dry fiberboard at the present time requires compliance with E1 emission limits of 6.5 mg/100 g for particleboard and 7.0 mg/100 g for fiberboard determined with the perforator method [24].

The formaldehyde emission values of MDF panels were determined according to EN 120 [25] standard. According to this standard, 100 g MDF samples (25 mm × 25 mm × 9.4 mm) weighed to the nearest 0.1 g were placed in the round bottom flask of the apparatus developed for this purpose. 600 ml toluene was added to this flask. About 1000 ml of distilled water was poured into the main extractor such that the water level was 1–2 cm below the siphon tube. The condenser and the gas absorption section were then connected. Some distilled water was also added to the conical flask of the absorption section to avoid any escaping formaldehyde. Extraction started with heating mantle, and continued for 2 h after the toluene first flowed back through the siphon tube. At the end of this period, the solution in the extractor was cooled to 20 °C, and transferred into a 2 l flask. The total volume was then made up to 2 l with distilled water.

The perforator value of the solution was determined using UV Spektrofotometre Specord 30. The result of the spectral analysis of the solution was calculated as milligrams of formaldehyde per 100 g of dry board.

3. Results and discussion

3.1. Mechanical properties of MDF panels

Since water in amine solution also added to the UF resin, fiber mats burst in pressing with PAS (1.4%), MAS (1.4%), and CPAS (1.2–1.4%). However, it did not burst with fiber mats for urea added to UF resin. Fig. 1 shows the values of the some mechanical properties of MDF panels produced with UF resin by adding different amine compounds.

When a US chemical was added to the UF resin, the MOR values of MDF panels decreased compared to control panels, as can be seen in Fig. 1. It was determined that MOR values of MDF panels produced in a higher ratio than 0.4% US addition to UF resin decreased significantly. According to the EN 622 [26] standard method, the quality necessities specified the value of MOR was $>25\ N/mm^2$ for the thickness of these MDF panels in this study. The modulus of rupture value of MDF panels was found above a specified EN value for these amine compounds, especially CPAS, PAS, and MAS chemicals. The highest value for MOR was observed in 0.4% CPAS addition to UF resin, and the increase in this value was 13.82% compared to control panel. It was concluded that the MOR values of these panels produced at a 16% rate of UF resin increased by 2.08%, 16.07%, 7.04%, and 7.85% by using 0.8% rate of ethylamine, propylamine, methylamine, and cyclopentylamine solution addition, respectively. Ebewele et al. [19] determined that the resistance of UF bonded joints to cyclic stress was substantially improved by modifying the resins through incorporating trifunctional urea-capped amines into the resin during synthesis or curing the resins with di- and trifunctional amine hydrochlorides. The lower stability and durability of UF resin is attributable to hydrolytic degradation and stress rupture. The structural factors responsible for these processes suggest that the stability and durability of a UF resin can be enhanced by modifying its structure to allow production of a cured resin with a more flexible structure and a more random distribution of cross links [20]. An added positive feature was the decrease in formaldehyde emission induced by decreased density of aminomethylene bonds along the chain of the resins to which the amines were introduced [2]. Consequently, the MOR values of MDF panels were improved by adding these amine chemicals.

Fig. 2 demonstrates the effect of some amine compounds on the internal bond strength of MDF panels. When used in 0.4% and 0.6% rates of US chemical addition to UF resin, it was determined that IB values of the MDF panels increased compared to those of the control panels. The IB values of MDF panels decreased slightly in a higher addition ratio than 0.8% for US chemical in UF resin, comparatively with control panel value. The IB values of MDF panels increased by the addition amine compounds to UF resin compared to EN standards (IB $>0.65\ N/mm^2$). The IB values of these panels ranged from 0.68 to $1.99\ N/mm^2$. The highest IB ($1.99\ N/mm^2$) value measured for these panels was produced using 0.4% rate of propylamine solution. IB values decreased with the increase in chemical solvent concentration in MDF panels. It was also determined that the IB values of these panels produced 16% rate of UF resin increase by 15.38%, 40.91%, 28.41%, and 32.31% using 0.8% rate of ethylamine, propylamine, methylamine, and cyclopentylamine solution addition, respectively. It was known that when the formaldehyde scavenger was added to UF resin, the mechanical properties of panels decreased. But, it was determined that the IB values of the all used amine chemicals were provided to increase depending on the lessened density of aminomethylene bonds along the chain of the UF resin.

As known, Ebewele et al. [19,20] found that the amines were incorporated in the UF polymer chain by direct reaction of the amine with urea and formaldehyde resin synthesis (1), by conversion of the primary amine group to its urea derivatives prior to reaction with formaldehyde to form the resin (2), and by conversion of the amine to its hydrochloride salt, which was then used instead of ammonium chloride as an acid curing agent (3).

$$H_2N–(CH_2)_6–NH_2 + NH_2CONH_2 + HCHO \rightarrow –NH–(CH_2)_6–NH–CH_2–NHCONH– \quad (1)$$

$$NH_2–(CH_2)_6–NH_2 + 2NH_2CONH_2 \rightarrow NH_2CONH–(CH_2)_6–NHCONH_2 + 2NH_3 \quad (2)$$

$$Cl^{-}\,{}^{+}NH_2–(CH_2)_6–NH_2^{+}Cl^{-} \quad (3)$$

The first modification eradicated resin reactivity and curing. The second and third types of modification gave, instead, resins of various curing reactivity, according to the amine used. These resins presented improved resistance to cyclic stress induced by moisture variations. A clear indication that the flexibility of these resins is an improvement over that of standard UF resins is in the fact that their tendency to crack and fracture was reduced [2,19,20]. The result of particleboard and wood joint cyclic stress testing of UF resins modified by 13% by mass hexametyhlene triamine, or 28% by mass poly(propyleneoxide)triamine showed that such a system had excellent stability even after repeated wet–dry cycles [2].

Fig. 3 shows the MOE values of MDF panels produced with UF resin added to some amine solutions in different concentrations. As rates of the US chemical concentration increased, the MOE values of these panels decreased similar to MOR values, comparatively

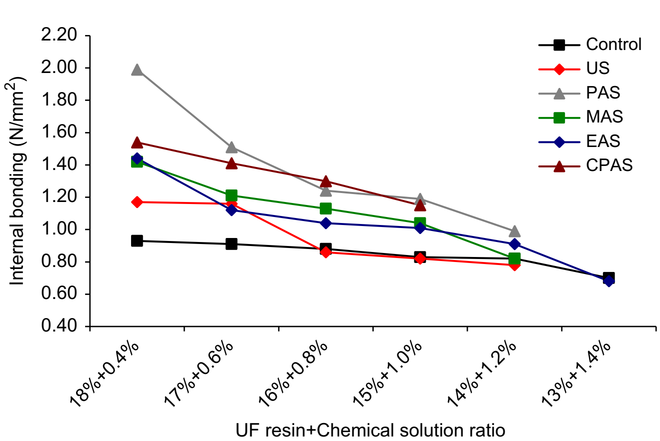

Fig. 2. Internal bond strength (IB) values of MDF panels.

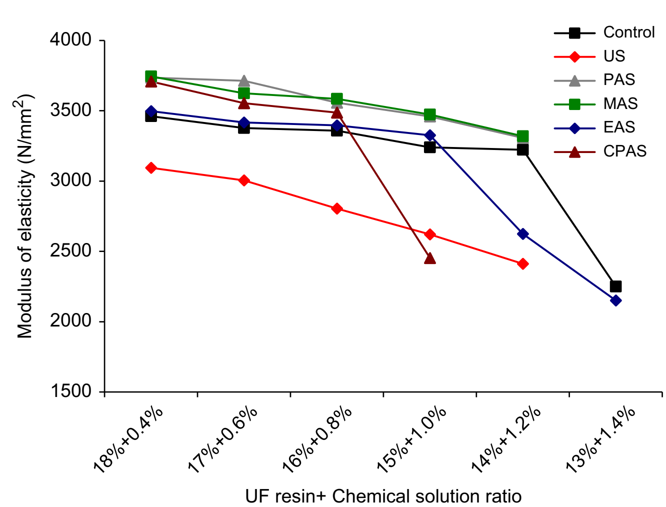

Fig. 3. Modulus of elasticity (MOE) values of MDF.

with the control panels. When PAS, MAS, EAS (except 1.2% and 1.4%), and CPAS (except 1.0%) chemicals were used in UF resin, it was determined that the MOE values of MDF panels were significantly much higher than those of the control panels.

Several researchers stated that while the low molar percentage level of addition used proved highly beneficial such modifications might become counterproductive if excessive amounts of amine were added. Thus, whereas flexibility and stress distribution were improved considerably, at the low levels of addition used, a significant increase in the resin of the proportion of each amine over that used by the researchers might reduce resin cross-linking and increase paracrystallinity to the extent that strength might begin to lessen. However, such probable disadvantages might well be overcome by increasing the formaldehyde/urea molar ratio to produce the lower formaldehyde emission obtainable with such amine-based modifications. In the future, amine modification might present possibilities even better than the excellent results already achieved and reported [2,19,20].

3.2. Physical properties of MDF panels

The changes in thickness swelling to MDF panels produced with UF resin added to some amine solutions in different concentrations are presented in Fig. 4. Depending on the amount of US concentration in MDF panels, TS values ranged from 6.24% to 11.28% higher than other panels. The TS values of MDF panels slightly increased with adding other amine solvent concentration to UF resin in these panels. The highest value for TS of MDF panel was determined in 1.2% US addition to UF resin. The minimal increases were found in the other used amine chemicals. The values of TS (24 h) were also determined as <12% for the thickness of all MDF panels. In this study, it was determined that the excessive amine chemicals usage resulted in a negative influence on the physical properties of MDF panels. The water absorption values of these panels showed similar increases to results of the thickness swelling.

Fig. 5 shows that water absorption values of MDF panels produced with UF resin added to different concentrations of urea chemical are much higher than control panels. However, the other amine chemicals have quite moderate results in terms of water absorption, compared to the control panels. The WA values of these panels for CPAS chemical ranged from 17% to 24.34%. The lowest WA value (15.72%) was obtained for the MDF panel including 0.4% PS chemical while the highest value was observed for the MDF panel including 1.2% US chemical. The results indicated that addition of these amine solution concentrations increased the WA values of these panels more than the control panels. However, it was observed that these amine chemicals, except urea, had a positive effect on the resistance to the water.

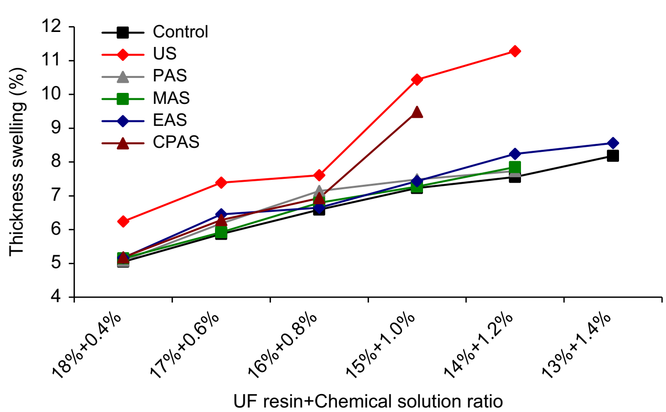

Fig. 4. Thickness swelling (TS) values of MDF panels.

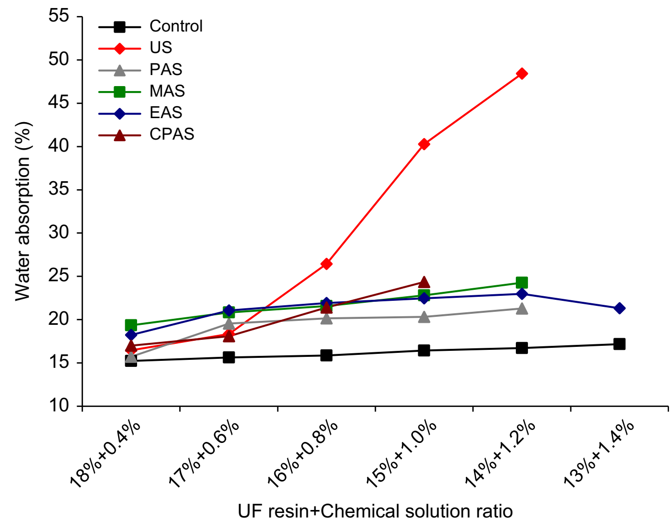

Fig. 5. Water absorption (WA) values of MDF panels.

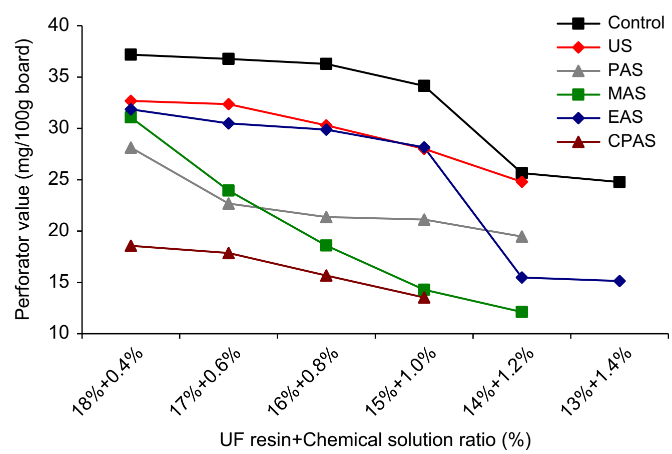

Fig. 6. Perforator values of MDF panels.

The chemistry of UF resins as regards their formaldehyde emission and water repellency has been approached differently from the methods outlined earlier. One approach includes long-chain aliphatic primary diamines in the UF resin skeleton. It is known that because the long alkyl chain connecting the two main groups was once included in the polymer backbone it will improve water resistance and flexibility in the cured UF resin network [2].

3.3. The perforator values of MDF panels

The perforator values of MDF panels produced with UF resin added to different concentrations of some amine chemicals to reduce formaldehyde are presented in Fig. 6. It also shows that the perforator values of control panels were acquired without any addition of amine chemical. When the ratio of US chemical increased to 0.4% or higher, it was determined that the US chemical was much more ineffective than other amine chemicals.

As shown in Fig. 6, the minimum perforator values were especially obtained from CPAS chemical. With the increase in these amine chemicals ratios in MDF panels, the perforator values decreased. It was determined that the reduction ratio of formaldehyde emission was much higher than other amine chemicals, when 0.8% of CPAS was added. The highest decrease in formaldehyde emission was 57% for CPAS to UF resin. It was thought that this outcome depended on the CPAS chemical, which had a cyclic structure unlike the other used amines. In addition, it was determined that PAS and MAS chemicals were more effective in decreasing formaldehyde emitted from MDF panels. The perforator values of MDF panels with PAS chemical ranged from 28.12 mg/100 g to 19.47 mg/100 g lower than the control panels. On the other hand, the perforator values of MDF panels with the increasing amount of MAS chemical decreased from 31.06 mg/100 g to 12.11 mg/100 g. The use of formaldehyde scavenger in UF resin ensured the reduction of formaldehyde and met the required EN standard in terms of the mechanical and physical properties. It was found that the formaldehyde emission of MDF panels produced at a 16% rate of UF resin decreased 16.5%, 41%, and 48% using 0.8% rate of ethylamine, propylamine, and methylamine solution addition, respectively. This result also showed that the use of these amine chemicals minimized the tendency of these panels to emit formaldehyde. The formaldehyde scavengers are used to decrease formaldehyde emitted from products such as boards and thermal insulation while minimizing the loss of cure speed and the loss of internal bond strength, modulus of rupture, and modulus of elasticity [27].

4. Conclusions

Some amine chemicals were used to decrease formaldehyde emitted from MDF panels in this study. As a result, the addition of CPAS chemical changing ratios to UF resin had considerably positive effects on the mechanical and physical properties of MDF panels, and ensured a reduction in the formaldehyde released from these panels. Using US chemical as a formaldehyde scavenger had less effect than other amine chemicals in terms of formaldehyde. In addition, the physical and mechanical properties of these MDF panels were adversely affected by US addition in UF resin. An addition of appropriate ratios of PAS and MAS chemicals provide values that are close to the required E1 value for perforator standard. These chemicals also provided the EN standard for the physical and mechanical properties. EAS chemical almost showed the same features as US chemical in decreasing the formaldehyde emitted from MDF panels, but it was concluded that the mechanical and physical properties of these panels were much higher in EAS chemical than in US chemical.

In conclusion, it was determined that the physical and mechanical properties of MDF panels improved by using different amine solutions in UF resin as formaldehyde scavenger, and the formaldehyde emission in MDF panels decreased. Thus, it is possible that these amine compounds can act as an alternative to decrease formaldehyde emitted from MDF in the future.

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