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尿素樹脂接着合板의 遊離포름알데히드 放散 제거 및 조절방법에 대한 比較研究

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Comparative Study on the Control and Removal of Formaldehyde for the Urea-formaldehyde Resin Bonded Plywood

— Adhesive control —

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要 約

尿素樹脂를 接着劑로 使用한 木質製品中 合板은 建築內裝 및 家具, 후래쉬도아, 마루판等 광범하고 다양한 용도로 住居環境에 使用되고 있다. 그런데 이러한 合板中 尿素樹脂接着層으로 부터 遊離 또는 分解되어 方出되는 포름알데히드는 有毒한 化学藥劑로서 극소량의 농축으로도 불쾌감, 頭痛 및 人體에 위험을 실제로 초래하고있다. 따라서 이러한 유리포름알데히드를 제거 또는 조절하여 소위 "포름알데히드 문제"를 解決하는 處理方法에 목표를 두고 脫포름알데히드效果 및 合板의 材質에 미치는 效果를 상호 比較하고 그 改善點을 밝히고자 하였다.

改良크로모트로핀酸方法으로 유리포름알데히드를 定量하였으며 주로 接着劑製造 및 混合에 중점을 두고 除去劑를 첨가할 때의 效果를 比較하였으며 塗布方法은 尿素處理에 限하였다. 結果는 다음과 같이 要約할 수 있다.

1. 尿素溶液침지처리와 硬化劑處理가 가장 좋은 유리포름알데히드放散除去效果를 가져 왔으며, 리조시놀4%, 알부민處理도 좋은 結果를 가져왔고 樹皮粉增量處理도 그 가능성이 있음을 볼 수 있다.
2. 合板接着強度는 常態接着強度에서 모든 處理가 전부 규격에 合格하며 특히 리조시놀2%와 尿素溶液沈漬處理가 월등히 높았고, 2類合板은수시험에 依한 接着強度는 硬化劑處理로만 不合格이고 리조시놀2%가 對比合板에 比하여 좋은 強度를 보였고 樹皮, 尿素處理가 對比 合板보다 強度가 높았다.
3. 處理合板의 氣乾含水率은 11～13% 사이로 모두 規格을 만족시켰다.
4. 리조시놀, 알부민과 尿素溶液沈漬處理의 混合效果는 계속 研究하면 더 좋은 結果를 획득하리라 사료된다.

SUMMARY

This study has been carried out to make a comparative study for the adhesive control methods specifically developed for application to formaldehyde. The method for formaldehyde determination used in this report is the improved chromotropic acid determination.

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The results are summarized as follows:

1. The soaking treatment in aqueous solution of urea took the most scavenging effect on the formaldehyde release from a plywood sample glued with a urea formaldehyde adhesive, and other removal treatment such as resorcinol, albumine-, and hardener-treatment gave significant reduction too.
2. In glue shear strength of dry test, 2% of resorcinol treatment and soaking treatment showed the highest strength and all the other treatment met the standard, but in hot water soaking test, 2% of resorcinol treatment gave the best results, on the other hand, adding the hardener showed the lowest strength and failed in meeting the standard.
3. Air dried moisture content of all treated plywood met the standard which calls for 13% or bellow.
4. In this comparative study, we can make a strong combination each other or go into the details of one treatment for the best result through the more study.

1. INTRODUCTION

The release of formaladehyde fumes from plywood bonded with ureaformaldehyde resins (U.F) is a problem which has been frequently studied.

Because, unfortunately, these U.F. adhesives have the inherent characteristics of giving off free formaldehyde which is a toxic chemical, during their use in the producing plant, and their storage or use of the resulting glued plywood.

Especially, the extensive utilization of Plywood for interior construction of habitable space has led to what is called the "Formaldehyde Problem" – a build up of the vapor to concentrations that are a nuisance, uncomfortable, or an actual health hazard.

The potential toxic effects of formaldehyde on the human body are clearly pointed out in general. (Patterson et al. [1976], Kitchens et al [1976])

It is an allergen, and highly toxic, causing eye and lung damage, and affecting the central nervous system.

At present in USA, the official limit is 3 parts per million (ppm), but NIOSH recomended lower levels; with maximum exposure to 1 ppm for any 3-minute period as a concentration of HCHO in air.

The human nose is extreamly sensitive to formaldehyde: formaldehyde detection is possible at 0.8 ppm (Walker, 1964).

So, the use of such products as plywood in home construction could result in exposure to people of all ages.

Now, We have to be interested in this problem in large degree.

Publications for the control and removal of formaldehyde may be regarded conveniently in two respects (1) During manufacture (2) afterwards, and also classified in terms of the type of control method: (1) Adhesive (2) Adsorbent (3) Coating (4) Ventilation.

Adhesive control is a parameter largely under control of manufacturer. At first urea-formaldehyde molar ratio (resin formulation) is very important to the resin manufacture. The free formaldehyde content was significantly increased by the HCHO/urea ratio in the range of 1.7 to 1.9, a factor of importance in the ordor problem.

Free formaldehyde content was linealy and positively correlated with the strength properties, under condition of low free formaldehyde cure rate is low and poor bonding results. (Hse, 1974).

Therefore standards are recommended for thre free formaldehyde concentration at 0.3 to to 1.0 percent (Temkina, 1974), and 8 major factors are listed as influencing the liberation of formaldehyde during manufacture and storage (Patterson, 1972).

At the second, by adding various materials to the urea formaldehyde adhesive binder, significant reduction of formaldehyde release has been obtained.

These additives are usually reactive to HCHO and act, therefore, as scavengers.

Thus Ginzel (1973) added ammonia and urea; Roffael (1975) also added hardner, $NH_4OH + NH_4CL$ + Urea; Minermure (1975) reduced the formaldehyde emission by the addition of melamine or potato protein plus urea;

Roffael included a phenolic resin; Kubitzky added a variety of compounds, amide or amine plus hide glue and several N-containing substances;

Sakarada (1973) treated the resin flour paste with NH_4OH, ammonia carbonate, sodium sulfite and hardener; and Kawahara (1973) added urea and flour (filler); Inui

(1974) used enzymes plus wheat flour; Ohhara(1974) treated capture agent polymer (Ammonium and/or amine) salt to the U-F resin. The reduction in formaldehyde evolved was 10-fold; Miwa (1974) added inorganic peroxide (H_2O_2) to U-F resin.

On the other hand, coating and ventilation methods could be used by either user or manufacturer.

In case of coating, plywood or veneer was treated with a varnish or a lot of salt-solution.

There are numerous references to the use of aqueous urea solutions to give a product with reduced free formaldehyde content. (Miwa, 1974, Kawahara 1974)

As a ventilation method, plywood was passed through a drying machine (at 80°C) into which air and NH_3 were brown (Yoshimitsu, 1973), The reduction in evolved HCHO was significant. Neusser and Zentner (1968) pointed out that "fumigation" with ammonia gas was used in Norway and Austria to eliminate formaldehyde odor librated from P.B. used in house construction.

Adsorbents which are cleaning agent for air could be largely a way for the user to deal with the odor; through a MnO_2-CuO mixed catalyst bed (Kobayagawa, 1974) or white clay plus 30 pct hydrazinium sulfate, through HCHO reactive compounds (aq. sol. of dicyandiamide) impregnated into porous volcanic rock (ohe, 1974), and with papers containing compounds reactive to formaldehyde being used to wrap plywood. (Miwa 1974).

Many qualitative solutions have been proposed, but there is a notable lack of quantitative information that permit an effective solution at "the end of the line"... i.e., after the material has been installed and found to be actively emitting formaldehyde at unacceptable rates.

This report is carried out to make a comparative study for the adhesive control methods specifically developed for application to formaldehyde.

2. Materials and Methods.

2.1 Manufacture of Plywood

(1) Wood species: Wood species used for veneer were Meranti. The thickness of the face veneer was 1.1 mm and that of core veneer, 2.2mm.

The specific gravity of meranti was 0.52 gr/cm^3 and its moisture content was conditioned in the range of 8 ± 1%.

(2) Adhesive: Urea-formaldehyde resin adhesive was used for a process of gluing plywood. Molar ratio (HCHO/Urea) was 1.6 and 1.5% of PVA was added to the formaline at the start of the manufacture of resin. The properties of urea-formaldehyde resin showed that solid content of the U.F resin was 53%, and pH of resin, 7.4. The quantity of glue spread for plywood was 280 gr/m^2.

(3) Pressing condition: For the manufacture of plywood, hot pressing conditions are as follows:
platen temperature; 120°C, specific pressure, 12 kg/cm^2, and time of heating, 90 seconds.

2.2 Treatment for removal of formaldehyde release.

(1) Plywood for control: As a filler, 10 percent of wheat flour and 0.5 percent of NH_4Cl as a hardener were added into the U.F. resin.

(2) Soaking treatment: Core and face veneers were soaked in the 30 percent of aqueous urea solution and then dried to the moisture content of 8%. The same process as the control plywood was applied.

(3) Hardener treatment: Additives which act as scavenger such as 3 percent of NH^4Cl + 1 percent of NH_4OH + 10 percent of urea were added to the resin.

(4) Bark filling: 10 percent of oak bark flour ($120^{\#}$-$180^{\#}$ mesh size) and 10% of water were added to the resin for the scavenging effect of the phenolic substances.

(5) Albumine treatment: 3 percent of Alubumine was added into the adhesive binder for the scavenging effect of protein.

(6) Resorcinol treatment: For the scavenging effect on the adding resorcinol into the resin, μ.F. adhesive confined from 1 percent to 4 percent of resorcinol.

2.3 Test Method for Formaldehyde Release

Clarmont (1976) et al described a simple procedure for determining the amount of "evaporable formaldehyde" evolved from μ.F resin bonded products which is ground first in a willy mill. The limit of detection was near 0.3-0.4 ppm. The apparatus used is shown in Fig. 1. Dry nitrogen gas from a commercial cylinder was passed

through the apparatus at 50ml/min, preheated by passing through a steel coil, and led into the sample vessel. The evolved formaldehyde was absorbed in chromotropic acid solution (sodium salt). Both coil and sample vessel were immersed in a constant temperature bath.

Samples of U.F. glued plywood were first ground in aminiatureWilly mill to pass a 20-mesh/inch screen and then conditioned to the about 8 percent of moisture content. About 1 gr samples were used at 25°C, and evolved formaldehyde was absorbed over a period of 3.5 hours.

The reagent-grade chromotropic acid (sodium salt) was used without any purification. A solution was prepared by dissolving 2.5 g of the salt in 25 mll of distilled water and filtering. One ml of water was placed in a glass-stoppered test tube approximately 18 by 150 mm and to this was added 1 ml of the chromotropic acid solution. Ten ml of concentrated sulfuric acid was carefully added with continuous shaking and cooling. This solution was used to absorb the evolved formaldehyde. After completion of the test, the test tube was stoppered and placed in boiling water for 30 minutes, followed by cooling and diluting with water to a volume under 100 ml in a volumetric flask. After further cooling, the solution was adjusted to 100 ml at room temperature. The absorbance of this solution was measured against a reagent blank at 570 mm.

A calibration curve was prepared using the above method. The exact concentration of the reagent-grade 37.0 percent formaldehyde solution was determined by the sodium sulfite method as outlined by Walker (1964).

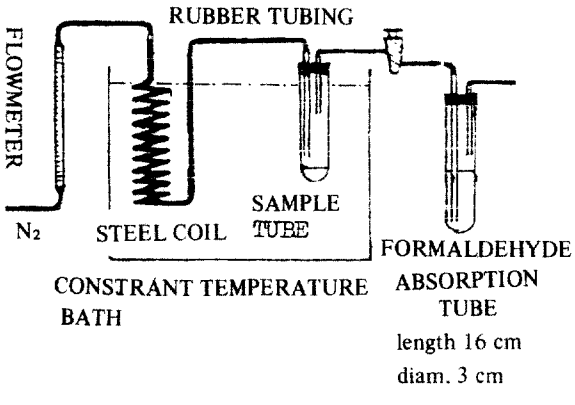

Figure 1. Apparatus used for the determination of formaldehyde evolution from plywood.

2.4 Glue shear test and moisture content of Treated plywood.

(1) Moisture content: After the plywood was left in air dry condition for one week, air dried moisture content of plywood was measured.

(2) Glue shear test: Glue shear stress was determined according to ASTM D 805-1963/66. For Plywood glue shear tests, the direction of grain in each face ply shall be parallel to the length of the specimen and the grain direction of the core shall be perpendicular to the length of the specimen (specimen B type).

The specimens were tested dry and they got tested after hot water soaking treatment (70°C ± 3°C in water for 3 hr, 60°C + 3°C drying for 3hr).

All strength is expressed in kg/cm^2 of shear area.

3. Results and Discussion

3.1 The effect of removal treatment on the formaldehyde release.

Factors such as the amount of formaldehyde used in this resins, the formulation of the resins, the amount of resin applied, the curing conditions, curing times used, resin formaldehyde cavengers the plate pressures during pressing, the duration of storage before use, and the environment and climate in which the final use is made may all affect whether formaldehyde release from a plywood will be so extensive as to make its use inadvisable. (plath, 1967, 68; Roffael, 1975)

This work has been carried out to obtain a good result with the conditions of as low molar ration (HCHO/Urea) as possiible, optimum pressing condition, and improved chromotropic acid determination.

The amount of formaldehyde evolved by improved chromotropic acid determination is more than that released to confined air by dessicator method. Therefore, this is the total capacity for the formaldehyde release at room temperature comparatively.

The effects of removal treatment on the formaldehyde release from a plywood sample glued with a urea formaldehyde resin is shown in Fig. 2.

Results are expressed in parts per million (ppm) based on ovendry sample weight.

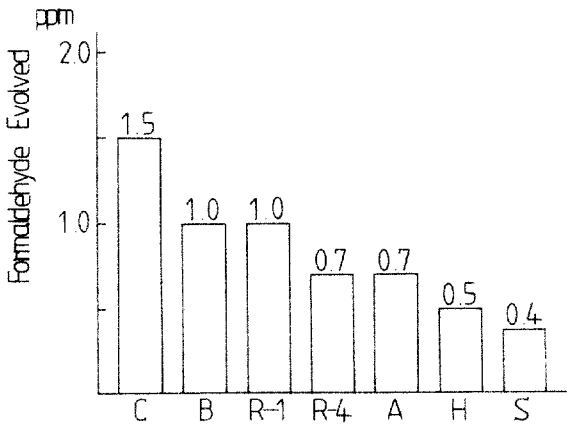

Fig. 2. The scavenging effect of removal treatment on the formaldehyde release.

C: Control
B: Bark
R: Resorcinol
A: Albumine 3%
H: Hardner
S: aq. urea sol. soaking

From the above results, we can convert these results into mg/m^3 unit.

Most of removal treatments excepting soaking treatment are additives which are usually reactive to free formaldehyde in the resin and function, therefore, as scavengers.

Aqueous urea soaking treatment and hardner treatment showed the most scavenging effect and other removal treatment gave significant reduction of formaldehyde release. There are numerous references to the use of urea to give a product with significant reduction of free formaldehyde content. (kawahara, 1974; Hojo, 1974; Kitakado, 1973; Miwa, 1974) The results turned out the same.

About the hardener, Roffael (1975) and Sakarada (1973) added hardner (NH_4OH + NH_4Cl + Urea), (NH_4 OH, ammonium carbonate,sodium sulfite and hardner) into the adhesive into the adhesive respectively. In this work, the combination effect of NH_4OH plus NH_4Cl plus urea has been examined and significant reduction has been gained also.

As a new methods for the control of free formaldehyde, albumine-and Resorcinol treatment gave good results. Protein-containing materials in numerous references are utilized for their apparent scavenging action for formaldehyde, (high; kubitzky, potato protein; Minemura, soybean flour; kidakado) but albumine has not been used.

Resorcinol is a phenolic substances but its reactivity is higher than that of phenol. Resorcinol-formaldehyde adhesive has a special property to set quickly at low temperature. Resorcinol added into the urea formaldehyde resin may be reactive to free formaldehyde during and other hot pressing, and act, therefore, as scavenger. (Lee, 1980)

In case of bark, the phenolic characteristics of bark extracts and physical fractions have attracted considerable effort aimed at making adhesive compositions, designed mostly for use in plywood and particle board manufacture (Hall; 1971, Harkin; 1971). Bark extracts can be and have been shown to make a acceptable goods on a small scale, but there has been no great industrial use of any of them. In this report scavenging effect of bark on the free formaldehyde has been studied, and 10% of oak bark flour shown better shear strength than that of without bark flour gave good scavenging results as shown in Fig. 2.

In this comparative study, we can make a strong combination each other or go into the details of one treatment for the best result through the more study.

3.2 Glue shear stress of plywood

Glue shear strengths are shown in Fig. 3 and Fig. 4, the results of dry test and hot water soaking test respectively.

In case of dry test, 2 percent of resorcinol treatment and aq. urea solution soaking treatment gave the highest shear strength significantly, and as a whole all the other treatment did not show any difference as compared with the control and satisfied the standard.

Adding resorcinol in the U.F resin showed the peak of strength at 2 percent and decreased the strength along its content (Lee, 1980).

In hot water soaking test, 2 percent of resorcinol treatment gave the best results, on the other hand, adding the hardner showed the lowest strength significantly at

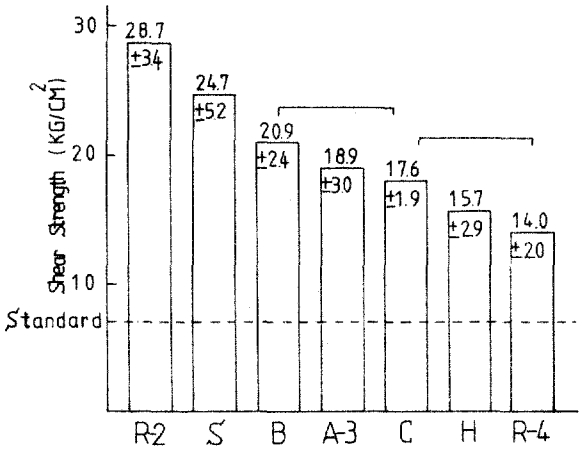

Fig. 3 Glue shear strength of dry test

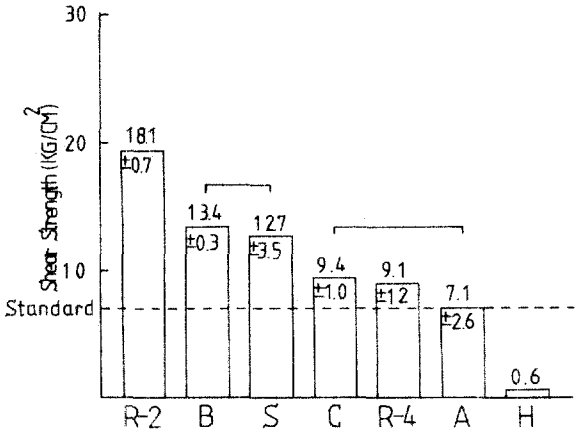

Fig. 4. Glue shear strength of hot water soaking test.

R: Resorcinol S: Soaking
A: Albumine-3% C: Control
B: Bark
H: Hardener
⎓ : Same group (5 % − LSD)

the 5% level of probability. The fail in meeting the standdard may be attiributed to a lot of content of NH_4Cl which liberate the HCl.

Roffael et al (1975) indicated that mechanical properties of particle board were affected negatively by omitting NH_4Cl from the hardener overcame this deficiency without negating the other advantage.

The upper group of control contains bark adding, and soaking treatment.

As a filler, Lee (1980) indicated that 10% of oak bark gave better shear strength than that of control in dry and wet test. This result is the same as shown in Fig. 3 and Fig. 4.

The residual group has the same strength on the basis of control.

3.3 Air dried moisture content of treated plywood

After the plywood was left in air drying condition for one week, air dried moisture content of plywood was measured as shown in Table 1. All results met the standard which calls for 13% or below.

Table 1. Air dried moisture content of treated plywood

4 replication

Treatment	Moisture content (%) (Mean + SD)
Control	12.4 + 0.36
Bark	12.6 + 0.58
Albumine	11.7 + 1.39
Hardner	12.7 + 0.38
Soaking	10.6 + 0.65
Resorcinol - 2%	12.1 + 0.96
Resorcinol - 4%	12.7 + 0.37

CONCLUSION

The results of this work have shown as follows:

(1) The soaking treatment in aqueous solution of urea took the most scavenging effect on the formaldehyde release from a plywood sample glued with a urea formaldehyde adhesive, and other removal treatment such as

resorcinol-, albumine-, and hardener-treatment gave significant reduction too.

(2) In glue shear strength of dry test, 2% of resorcinol treatment and soaking treatment showed the highest strength and all the other treatment met the standard, but in hot water soaking test, 2% of resorcinol treatment gave the best results, on the other hand, adding the hardener showed the lowest strength and failed in meeting the standard.

(3) Air dried moisture content of all treated plywood met the standard which calls for 13% or bellow.

(4) In this comparative study, we can make a strong combination each other or go into the details of one treatment for the best result through the more study.

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