Activation of Wood Surface by Corona Treatment to Improve Adhesive Bonding

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SYNOPSIS

Oxidative activation of resinous wood surfaces by a corona treatment to improve adhesive bonding was studied. It was found that the wettability of the veneers, including hardwoods, softwoods, and tropical woods increased with an increase in the degree of treatment, and the gluability increased rapidly after the initial mild treatment. To elucidate the nature of any chemical change occurring on the wood surface, the dyeing examination of the wood and its components with Schiff's reagent was made, and the results showed a higher dyeing ability for corona-treated samples compared to untreated ones, indicating that aldehyde groups increased by the corona treatment. The treatment affected the alcohol-benzene extractives, and oxidized them to produce aldehyde groups. Especially, the neutral fraction in the extractives was significantly affected. On the other hand, negligible chemical effects of the treatment on the surface modification of the wood's main components were seen. Both the untreated and corona-treated samples adsorbed basic dye to the same extent of coloration. Thus, no measurable carboxyl groups increased on the surface of the samples. It seems that an increase in the wettability of corona-treated wood veneers resulted mainly from the oxidation of the high hydrophobic surface layer of neutral fraction substances in the extractives, and from the reduction in their hydrophobicity.

INTRODUCTION

Wettability or intimate contact of a liquid adhesive to a solid substrate is necessary for durable bonding. The bond quality between a paint and a solid surface is also affected by the wettability. Some wood species, however, contain extractives that interfere with the adhesive bonding of wood to other materials. They consist of hydrophobic resins, esters of fatty acids, waxes, etc. These substances form a structure of low surface energy at the wood surface. For this reason, many papers concerning the pretreatment of wood to improve its wettability and adhesive bonding have been reported. Oxidative activation of a wood surface is a useful method for improving adhesive bonding.[1] Corona discharge pretreatment is one of the interesting techniques for surface modification of polymers and is commonly used in the plastic film industry.[2-4] It has been reported that the treatment of the surfaces of wet pulp sheets in a corona discharge significantly improved the plybond strength of the paperboard obtained when the treated wet pulp sheets were laminated together, pressed, and then dried.[5] The treatment with corona was used to improve the gluing of resinous wood.[6]

The purpose of the present work was to apply such a corona pretreatment to improve the wettability of the resinous wood veneer and, consequently, its gluability with water-based adhesive. In addition, some experiments concerning the chemical effects of the corona treatment on the surface modification of wood veneer and its components such as cellulose, lignin, and alcohol–benzene extractives were made using dye-adsorption methods.

EXPERIMENTAL

Veneers and Their Extractives

As mentioned above, wood contains many different kinds of extractives, and their quantities differ in

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different woods. It is considered that the effect of corona treatment of wood on the wettability and the gluability might differ in woods. Thus, 18 kinds of factory-made sliced or rotary veneers from various wood species, as listed in Table I, were used in this study. The thickness of these veneers ranged from 0.2 to 2.5 mm. The content of their extractives were measured by extracting with an alcohol–benzene solution for 8 h.

The extractives from Japanese red pine were fractionated by two procedures. The first procedure is as follows: The alcohol–benzene extractives were poured into ethyl acetate and divided into solubles and insolubles. The soluble fraction was further fractionated as shown in Scheme 1 to afford the acidic fraction, the phenolic fraction, and the neutral fraction. The other method is as follows: The extractives from the wood meal were partitioned by successive extraction with n-hexane, ethyl ether, acetone, and methyl alcohol.

Hemicellulose from beech (*Fagus crenata* Bl.) and Japanese cedar (*Cryptomeria japonica*) were prepared by the Wise method,[7] and Brauns native lignin (BNL)[8] from spruce (*Picea* spp.) and milled wood lignin (MWL)[9] from Japanese red pine (*Pinus densiflora*) prepared in the usual way were also used in this study.

These wood components were impregnated on filter paper and then corona-treated. The procedure of the impregnation was as follows: Weighed filter papers (Toyo Roshi, No. 4) were dipped momentarily in the solution of extractives or each fraction, then drained to remove excess solution and dried. The papers were reweighed to obtain the weight of the impregnant. The veneer and the impregnated paper samples were conditioned at 65% relative humidity for 5 h prior to the corona treatment.

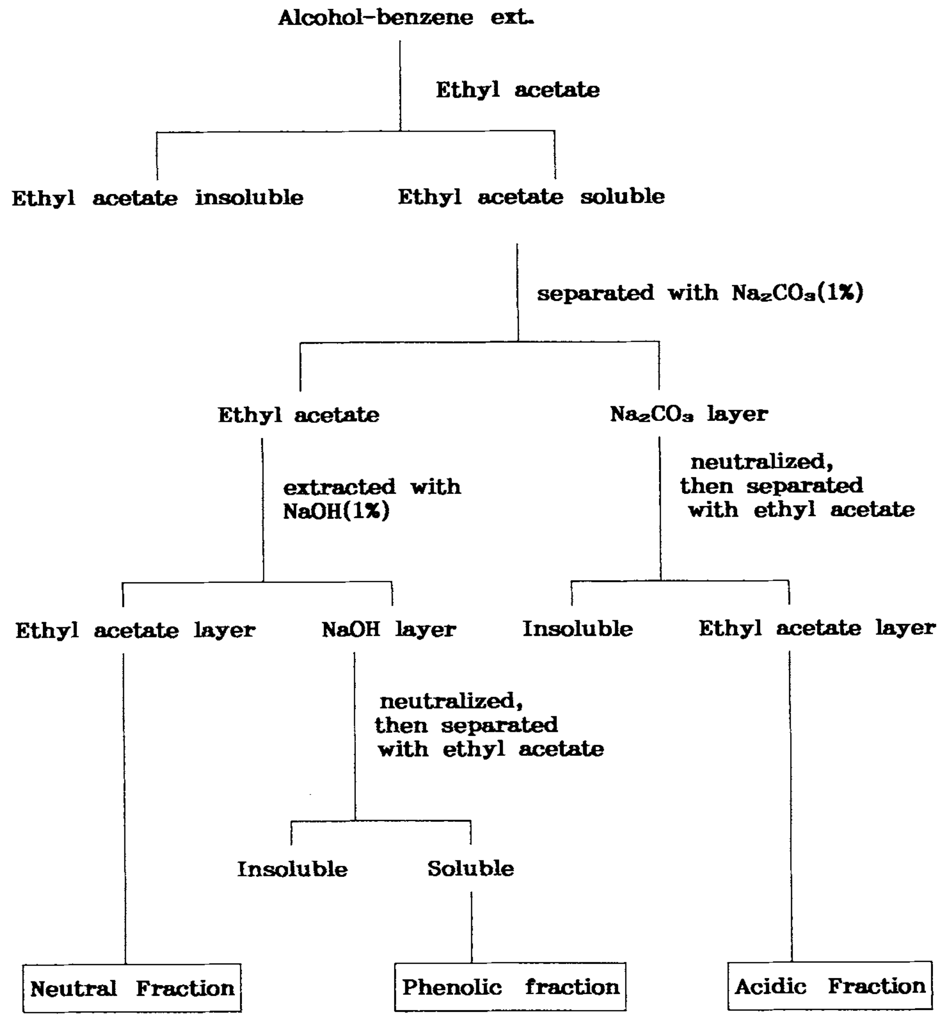
Corona Treatment

Figure 1 shows the corona-treatment apparatus used in this study. This apparatus consists of a high-frequency generator with a maximum of 500 W and 16 kV at 5 kHz and a treater station assembly that includes a grounded roll electrode covered with a dielectric layer of silicon rubber and an electrode made of stainless steel. The gap between the two electrodes was adjusted to 3.2 mm. The veneer or the impregnated paper specimens on the glass plate were treated by transporting them through the co-

Table I The 18 Wood Veneers of Domestic and Tropical Origin Used in This Study

Wood Species	Veneer	Thickness of Veneer (mm)	Extractive[a] (%)
Japanese larch (*Larix leptolepis*)	Rotary	2.00	2.2
Japanese red pine (*Pinus densiflora*) I	Sliced	0.60	3.5
Japanese red pine (*Pinus densiflora*) II	Sliced	1.00	14.7
Japanese oak (*Quercus crispula*)	Sliced	1.00	2.3
Teak (*Tectona grandis*)	Sliced	1.00	8.1
Merkus pine (*Pinus merkusii*)	Sliced	0.25	35.5
Japanese red birch (*Betula maximowicziana*)	Sliced	0.25	1.1
Japanese elm (*Ulmus davidiana*)	Sliced	0.35	1.0
Port Orford cedar (*Chamaecyparis lawsoniana*)	Sliced	0.30	2.3
Red lauan (*Shorea* spp.)	Rotary	2.00	2.0
Isunoki (*Distylium racemosum*)	Sliced	0.25	7.6
Mizume (*Betulaceae grossa*)	Sliced	2.50	2.4
Hinoki cypress (*Chamaecyparis crispula*) I	Sliced	0.30	4.9
Hinoki cypress (*Chamaecyparis crispula*) II	Sliced	0.30	3.9
Meranti (*Shorea* spp.)	Rotary	2.00	6.4
Zelkova (*Zelkova serrata*)	Sliced	0.35	3.1
Kapur (*Dryobalanops* spp.)	Rotary	2.00	3.2
Apitong (*Dipterocarpus* spp.) I	Rotary	3.50	1.7
Apitong (*Dipterocarpus* spp.) II	Rotary	3.50	8.9
Walnut (*Juglans nigra*)	Sliced	1.00	5.2
Purpleheart (*Peltogyne* spp.)	Sliced	0.20	11.5

[a] Alcohol–benzene (1 : 2) extractive.



Scheme 1

rona discharge field. The degree of treatment is shown in the following equation:

$$\text{Degree of treatment} = \frac{W}{V \times L}\ (W \times \text{min/m}^2)$$

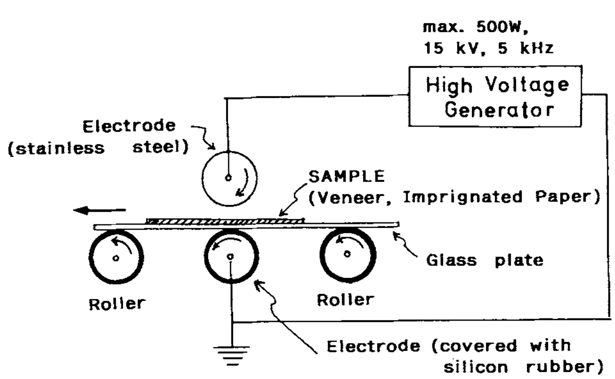


Figure 1 Diagram of corona-treatment apparatus.

where W is the electric power (W), V is the speed of treatment (m/min), and L is the length of the electrode (m), a constant of 0.5 m.

Measurement of Wettability

Wettability of the corona-treated and untreated samples was measured as the contact angle of a droplet of urea resin solution using a goniometer-type contact anglemeter (Model G-1, Erma LTD., Tokyo, Japan) at room temperature.

Glue Joint Strength

To explain the joint strength of the veneer compared to solid wood, the veneers were bonded to a 10 mm-thick sakura wood (*Prunus* spp.) block. This wood block was used as a strong material. The veneer of isunoki or purpleheart wood that was glued to the wood block with a mixed resin of urea–formaldehyde and poly(vinyl acetate) emulsion at a ratio of 1 : 2. The glue spread was 200 g/m^2. The 2-ply assemblies were pressed for 90 s at 110°C and at 0.5 MPa. The tensile strength perpendicular to the surface was measured.

Dye Adsorption

The chemical effects of the corona treatment were examined using of a dye-adsorption method described in a previous paper.[5] The dye adsorption of corona-treated samples was carried out after being evacuated and purged with nitrogen to remove ozone and other attached substances.

Schiff's reagent was used for detecting the presence of aldehyde groups. Schiff's reagent and a sulfurous acid rinse solution were prepared by the method described by Lison.[10] The specimen was treated in this reagent for 30 min, rinsed twice with sulfurous acid solution, and then washed with water. The spectral reflectance of the dyed specimen compared to that of an untreated one at the absorption maximum of the color of the Schiff's reagent–aldehyde adduct at around 560 nm, ΔA, was determined with a Hitachi double-beam spectrophotometer equipped with an integrating sphere. In the case of detecting the presence of acid sites (carboxyl groups), methylene blue was used. The specimen was treated with a methylene blue solution buffered to pH 8 with diethyl barbituric acid according to Tappi standards.[11]

RESULTS AND DISCUSSION

Changes in Wettability

The effect of the degree of treatment during the corona discharge on the wettability of the veneers was

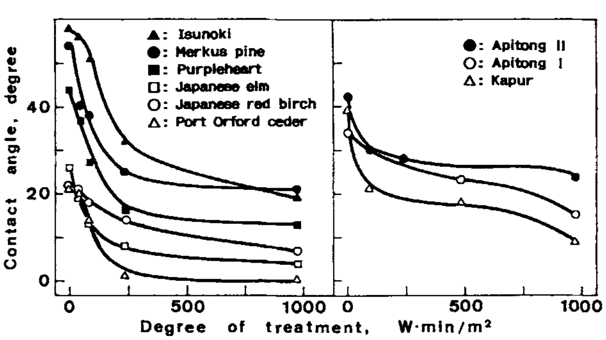


Figure 2 Variation of contact angle for the veneers with degree of corona treatment.

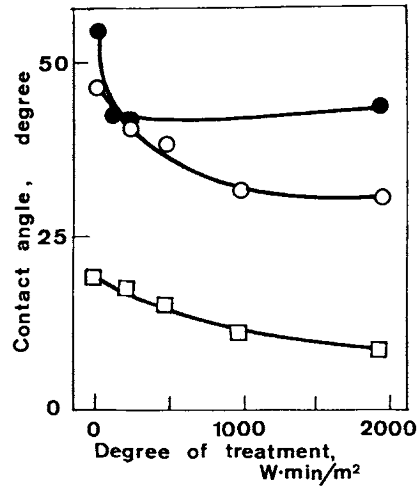


Figure 3 Effect of degree of corona treatment of veneer (O) before and (□) after extraction with alcohol–benzene and (●) its extractives from Japanese red pine on their contact angle.

measured by the contact angle of a droplet of urea–formaldehyde resin. Some of the results are shown in Figure 2. Veneer wetting by the droplet increased substantially with an increase in the degree of treatment.

The contact angles of the wood veneers were classified into three groups: A group of samples from isunoki, merkus pine, resinous apitong II, Japanese red pine II, and purpleheart that contained extractives of 7.6, 35.5, 8.9, 14.7, and 11.5%, respectively, originally had contact angles greater than 40°. Because of the corona treatment, their contact angles, however, decreased to around 20°, equal to those from the wetting woods. The contact angles for Japanese elm, Japanese red birch, Port Orford cedar, zelkova, and hinoki cypress, which had contact angles less than 30° and were originally wetting woods, decreased further with an increase in the degree of treatment. The contact angles of the veneers originally between 30° and 40°, such as meranti, kapur, and apitong I, showed intermediate properties between poorly and well-wetted woods. The woods that contained alcohol–benzene extractives of more than 5–7% generally had poor wettability for the urea resin droplet. Those that contained extractives of less than 4% were well wetted. The wettability of their veneers was improved significantly by the corona treatment.

The relationship between degree of corona-discharge treatment and contact angle for Japanese red pine is illustrated in Figure 3. The contact-angle values for the untreated samples gave the following order in decreasing wettability: First was the extracted wood surface with alcohol–benzene, next was the original wood surface, and the poorest wetting samples was the impregnated paper with alcohol-benzene extractives. The wettability of the impregnated paper increased with an increase in the degree of corona treatment, with similar curves being obtained for the extracted wood veneer. Extraction significantly increased the wetting of veneers. These results indicate that the wettability of the wood veneer was influenced by the content and quality of extractives in woods and was significantly improved by the chemical modification of the extractives with corona treatment.

Glue Joint Strength

The effect of the degree of treatment during the corona treatment on the glue–veneer bond strength measured by the tensile strength perpendicular to the surface is shown in Figure 4. The joint strength increased rapidly after the initial mild treatment of corona, but then steadily (isunoki) or gradually decreased (purpleheart). The gradual decrease in the joint strength induced by the prolonged treatment as shown for purpleheart may be due to an excessive degrading of the surface of the veneer. After a mild corona treatment, the increase in the joint strength for the glue–veneer bond corresponded to the decrease in their contact angle.

Surface Chemical Change Detected by Dye Adsorption

As mentioned above, the corona treatment of a wood surface can cause a considerable increase in the wettability and gluability of the resinous wood veneer. In connection with the cause of the remarkable effect observed in this work, some experiments were then carried out to elucidate the nature of any chemical change occurring on the wood surface.

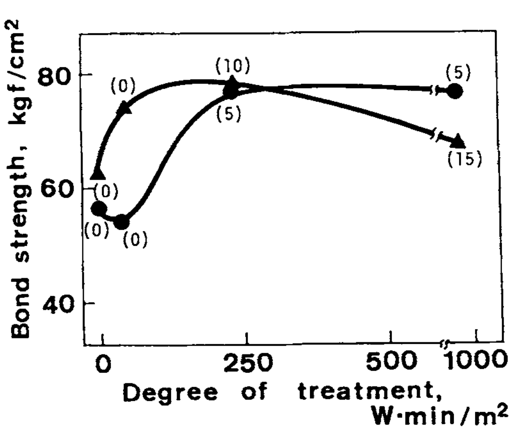


Figure 4 Variation of bond strength with degree of corona treatment. The values in parentheses are wood failure: (●) isunoki; (▲) purpleheart.

Table II Dye Ability Changes of the Wood Veneers during Corona Treatment

Wood Species	Absorption Increament (ΔA)[a] Dyed with Schiff's Reagent	Dyed with Methylene Blue
Japanese larch	0.221	0.044
Japanese red pine I	0.185	0.014
Japanese oak	0.163	0.039
Teak	0.261	0.013
Merkus pine	0.268	0.003
Japanese red birch	0.194	0.031
Japanese elm	0.228	0.002
Port Orford cedar	0.287	0.041
Red lauan	0.218	0.011
Isunoki	0.113	0.063
Mizume	0.239	−0.047
Hinoki cypress II	0.115	0.006
Zelkova	0.184	0.003
Walnut	0.098	0.021

[a] Absorption increament (ΔA): The absorption difference between the absorption of the corona-treated-dyed specimen and that of the untreated one.

It is important to note that the chemical change induced by corona treatment will be restricted to the surface and does not appear to affect the bulk properties of the wood. Therefore, the chemical effects were examined by the application of a dye-adsorption method that is used widely in the field of histochemistry.

The changes in the functional groups were examined to clarify the extent of oxidation, if any, of the wood surface during corona treatment. If corona treatment increases the number of aldehyde groups in the wood, the treated wood should show an increase in the adsorption ability for Schiff's reagent. If the surface oxidation of wood proceeds further, the carboxyl groups that can be detected by the increment of the basic dye adsorption ability such as methylene blue should increase. The extent of coloring of the dyed sample with the corona treatment can measure the spectral reflectance of it compared to that of a corona-untreated one at the absorption maximum of the color using a spectrophotometer with an integrating sphere.

It is well known that ordinary aliphatic aldehyde groups with Schiff's reagent develop a reddish violet color and exhibit an absorption maximum at around 560 nm. The corona-treated veneers adsorbed Schiff's reagent, and the extent of coloring changed with the corona treatment as shown in Table II. The results clearly showed a higher dye ability for the corona-treated veneer compared with the untreated, indicating that aldehyde groups increased with increase in the degree of corona treatment.

To elucidate the effect of wood components on the color development of the sample with Schiff's reagent during the corona treatment, the components such as hemicellulose, lignin, and alcohol–benzene extractives were isolated and then adsorbed Schiff's reagent before and after corona treatment. The extent of the coloring changes for the dyed samples subjected to corona treatment is shown in Table III. The values of the differences in the absorption, ΔA, for the filter paper for a cellulose sample, hemicelluloses, and lignins were small with values of about 0.08. These results indicated that aldehyde groups increased only slightly in the wood's main components such as cellulose, hemicellulose, and lignin during the corona treatments. On the other hand, the ΔA values for the alcohol–benzene extractives were greater, being 0.11–0.48, though these values for the extractives from different woods had different values. It seems that the chemical compositions of the extractives affect the values.

Incidentally, both the untreated control and the corona-treated veneers adsorbed methylene blue to the same degree of coloration. Thus, the absorption increment of the dyed samples, ΔA, was very small, as shown in Table II. Similarly, no absorption increment in methylene blue for the isolated wood components with the corona treatment are shown except for a small increment in that for the lignin. It is clear that no measurable acidic sites such as

Table III Effect of Corona Treatment of Wood Component on the Dye Ability with Schiff's Reagent

Sample	Amount Impregnated (%)	Absorption: Corona Treated (A)	Absorption: Untreated (B)	Absorption Increment with Corona Treatment (A) − (B)
Cellulose	0.0	0.208	0.120	0.088
Hemicellulose				
Japanese beech	5.7	0.239	0.167	0.072
Japanese cedar	5.6	0.264	0.197	0.072
Lignin				
BNL	7.5	0.496	0.418	0.078
MWL	7.5	0.600	0.510	0.090
Extractive[a]				
Japanese larch	5.9	0.807	0.330	0.477
Japanese red pine I	6.5	0.727	0.302	0.425
Japanese oak	5.7	0.820	0.432	0.388
Teak	6.4	0.640	0.268	0.372
Merkus pine	6.0	0.782	0.417	0.365
Japanese red birch	5.9	0.620	0.284	0.336
Japanese elm	6.3	0.688	0.367	0.321
Port Orford cedar	6.1	0.611	0.292	0.319
Red lauan	5.6	0.527	0.218	0.309
Isunoki	5.4	0.525	0.225	0.300
Japanese red pine II	6.2	0.491	0.267	0.224
Mizume	5.8	0.557	0.338	0.219
Hinoki cypress I	5.9	0.463	0.245	0.218
Meranti	5.1	0.486	0.289	0.197
Hinoki cypress II	5.7	0.495	0.322	0.173
Zelkova	5.2	0.431	0.261	0.170
Kapur	4.8	0.359	0.191	0.168
Apitong II	6.2	0.377	0.211	0.166
Walnut	4.9	0.570	0.462	0.108

[a] Alcohol–benzene (1 : 2) extractive.

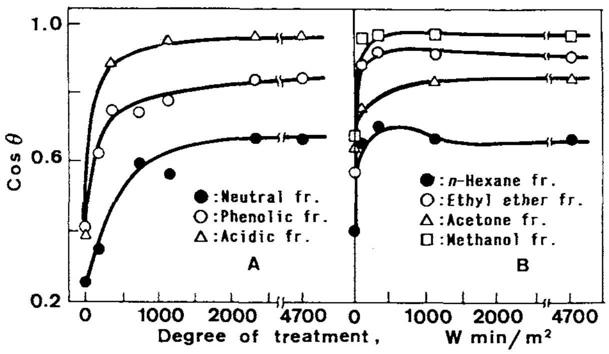


Figure 5 Effect of the corona treatment of various fractions of extractives from Japanese red pine on their wettability: (A) fractionation method; (B) successive method.

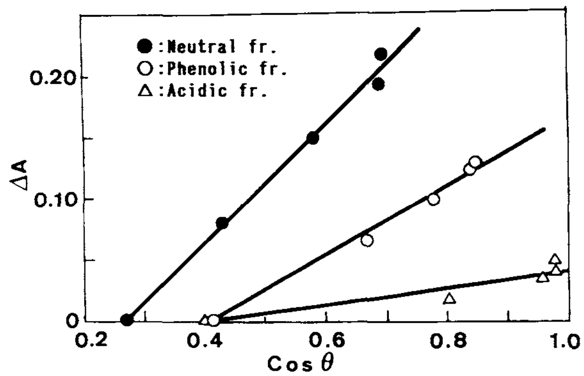


Figure 7 Relation between ΔA for the fractions of extractives from Japanese red pine and their cos θ.

carboxyl groups increased on the wood veneer during the corona treatment. These results agree with the earlier findings that cellulose is oxidized to produce aldehyde groups and not carboxyl groups by the corona treatment.[5,12]

Relation between the Wettability and the Dye Ability of the Extractives

The treatment of extractives by corona cause a considerable increase in the amount of aldehyde groups. Because of the corona treatment, the contact angle decreased with an increase in the degree of treatment.

What components in the extractives are the cause of this remarkable effect? The extractives from Japanese red pine were fractionated, and then each fraction was subjected to corona treatment. Figure 5 shows the effect of the corona treatment of the various fractions on their wettabilities. Both the neutral fraction and n-hexane fraction have a low cos θ value before corona treatment, because of their low polarity and hydrophobic natures. But during the early stage of corona treatment, their wettability improved significantly and then remained unchanged.

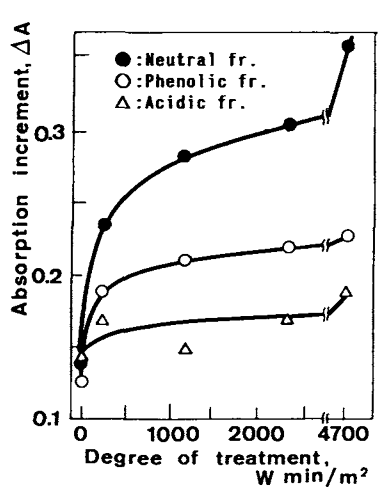


Figure 6 Relation between the degree of treatment for the fractionated extractives from Japanese red pine and the absorption increment (ΔA) dyed with Schiff's reagent.

The effect of the degree of corona treatment on the absorption increment for the dyed fractions with Schiff's reagent is shown in Figure 6. The ΔA values of the neutral fractions were much greater than those of other fractions for any degree of corona treatment. The relation between the ΔA and the wettability expressed as cos θ of the fractionated extractives are shown in Figure 7. These ΔA values were correlated by straight lines in cos θ plots, but their slopes differed. That of the neutral fraction was larger than those of the others. This indicates that the neutral fraction was significantly affected by the corona treatment.

CONCLUSION

The present paper has shown that the treatment of the surface of resinous wood veneers by a corona treatment causes a considerable increase in the wettability of the surface and, consequently, in the gluability of the veneers to water-based adhesives.

Negligible chemical effects of the corona treatment on the surface modification of the wood's main components, such as cellulose, hemicellulose, and lignin, evaluated with the aid of the dye-adsorption method were seen. On the other hand, the corona treatment affected the alcohol–benzene extractives and oxidized them to produce aldehyde groups. The neutral fraction in the extractives especially was significantly affected by the treatment. The substances in the neutral fraction contain a benzene ring and a double-bond structure in the molecules and originally have a high hydrophobic nature.

In conclusion, it seems that an increase in the wettability of corona-treated wood veneers resulted mainly from the oxidation of the high hydrophobic surface layer of the neutral fraction substances in the extractives and from the reduction in their hydrophobicities.

REFERENCES

1. E. L. Back, *Forest Products J.*, **41,** 30 (1991).
2. C. Y. Kim, J. Evans, and D. A. I. Goring, *J. Appl. Polym. Sci.*, **15,** 1365 (1971).
3. C. Y. Kim, G. Suranyi, and D. A. I. Goring, *J. Polym. Sci. C*, **30,** 533 (1970).
4. C. Y. Kim and D. A. I. Goring, *Pulp Paper Mag. Can.*, **72,** T-363 (1971).
5. I. Sakata, M. Morita, H. Furuichi, and Y. Kawaguchi, *J. Appl. Polym. Sci.*, **42,** 2099 (1991).
6. T. Uehara and T. Goto, *J. Adhes. Soc. Jpn.*, **20,** 333 (1984).
7. L. E. Wise, M. Murphy, and A. A. D'Addieco, *Paper Trade J.*, **122,** 35 (1946).
8. F. E. Brauns, *J. Am. Chem. Soc.*, **61,** 2120 (1939).
9. A. Björkman, *Svensk Papperstidn.*, **59,** 477 (1956).
10. T. Imaizumi, in *Histochemistry and Cytochemistry* (translated from L. Lison, *Histochemie et Cytochemie Animales,* Gauthier-Villars, Paris, 1960), Hakusuisha, Tokyo, 1962, p. 666 (in Japanese).
11. TAPPI Standard Method T237-sm: *Tappi,* **45,** 142A (1962).
12. T. Uehara and I. Sakata, *J. Appl. Polym. Sci.*, **41,** 1695 (1990).

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