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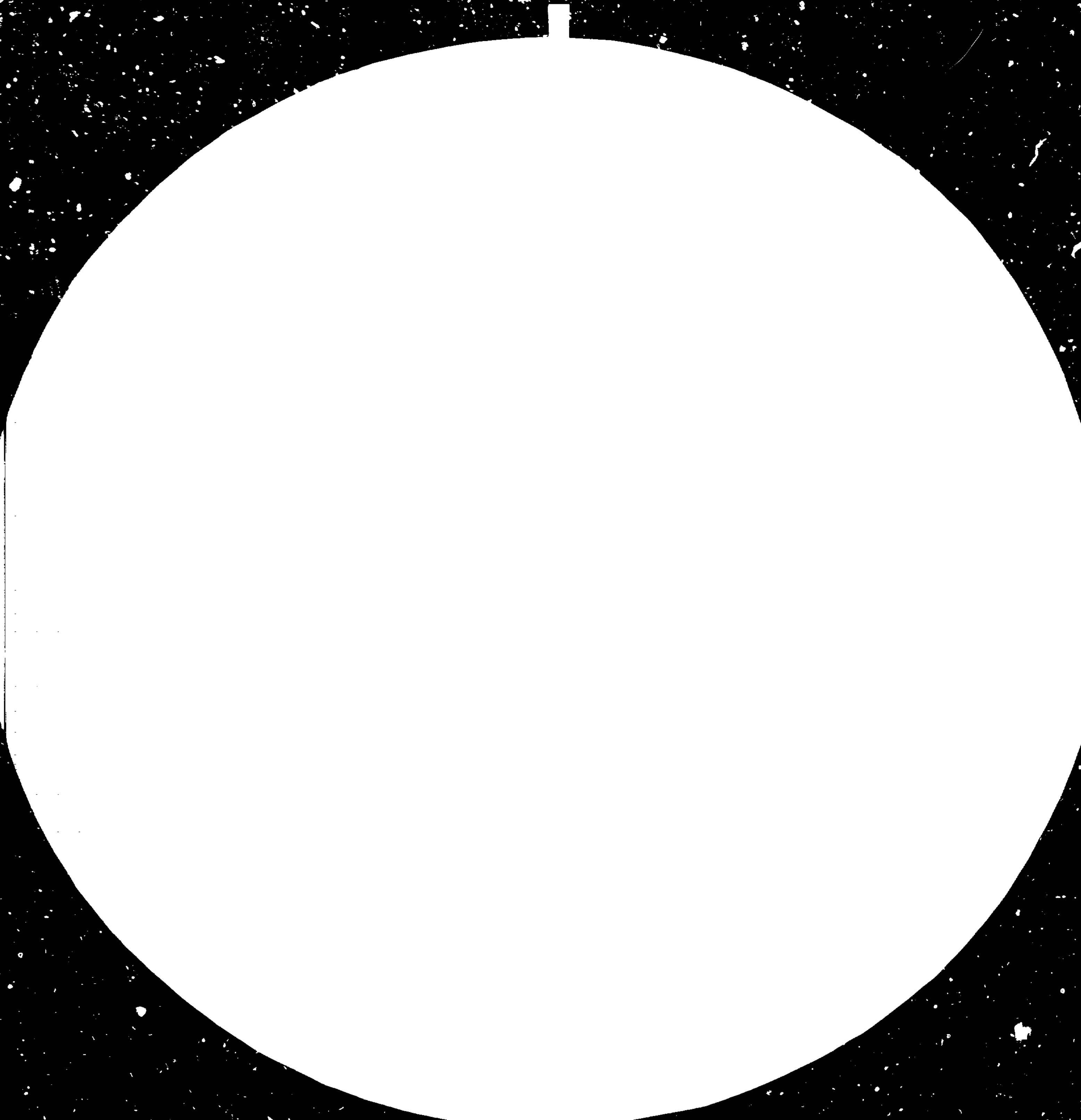

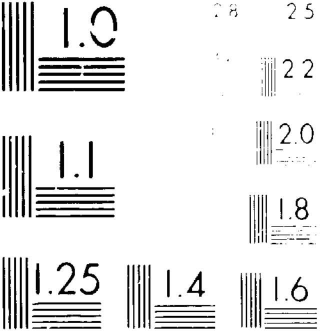
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SUPPLEMENT TO "ANNOTATED BIBLIOGRAPHY ON THE RESEARCH DONE ON THE USE OF NATURALLY OCCURRING ADHESIVES FOR WOOD PROCESSING INDUSTRIES"*

by

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TABLE OF CONTENTS

****

1. GENERAL

1.1 Glues in general

1. Dhingra, K.C., Rastogi, S.C., and Goel, R.K.
Handbook of adhesives: Manufacture and use of adhesives.
Small Business Publications, Delhi, 1973, pp.294.

The three sections of the book deal with (1) adhesives - their classifications, uses and manufacture, (2) adhesive formulations, (3) industrial uses of adhesives.

2. Mastow, P.
Chemical materials for construction: Handbook of chemicals for concrete, flooring, caulks and sealants, epoxies, latex emulsions, adhesives, roofing - water proofing, technical coatings, and heavy construction specialities.
Structures Publishing Co., Farmington, Michigan, 1974, pp.570.

3. Motoki, I.
Durability of adhesives.
Hyomen,12, No.9, 1974, p.537-44 (Jap.).

The bonding mechanism and the properties related to the durability of adhesives are reviewed.

4. Imoto, M.
Progress in adhesives.
Nippon Satchaku Kyokai-Shi,11, No.4, 1975, p.192-202.

5. Goel, R.K., and Gupta, R.K.
Industrial Adhesives and gums.
Small Business Publications, Delhi, 1976, pp.287.

The book gives a large number of adhesive formulations and a chapter on "Adhesives in wood industry" briefly describes natural adhesives used for wood and plywood.

6. Imoto, M.
Adhering: Adhesion and adhesives.
Kagaka Kyoiku,24, No.1, 1976, p.33-39 (Jap.).

A review on adhesives.

7. Shields, J.
Adhesives handbook, Ed.2.
Newnes-Butterworth, London, 1976, pp.370.

This book is a comprehensive reference work on the wide variety of adhesives materials and their usage as bonding agents. It is mainly concerned with the properties of adhesives and covers essential factors involved in adhesive bonding. The mechanical, physical and chemical properties of adhesives are comprehensively summarised in tables to assist in ready selection of adhesives for bonding a wide variety of materials.

8. Fukuzawa, K.
Adhesive technology: Part X.
Setchaku, 21, No.3, 1977, p.103-6 (Jap.).

A general review on adhesives.

9. Roy, D.C., and Chowdhari, S.
Identification of plywood glues.
IPIRI J., 7, No.1, 1977, p.10-4.

Twenty seven glue formulations were prepared and tested for identification on the basis of the fumes evolved on heating. The colour of the adhesives, pH of the fumes, odour and flame colour are tabulated.

10. Skiest, I.
Handbook of adhesives, Ed 2.
Van Nostrand Reinhold, New York, 1977, pp.1018.

Covers natural and synthetic adhesives and provides information on preparation of adhesives and sealants. The book contains 56 chapters contributed by 75 specialists in polymers, adhesives and bonding.

1.2 General wood working glues

11. Laval, G.
Colles et collages dans l'industrie du bois.
Compagnie Francaise d'Editions, Paris, 1968, pp.434 (Fr.).

The 12 chapters in the book deal with different aspects of natural and synthetic adhesives for gluing plywood and particle boards.

12. Glues in the wood industry.
    Cahier, Centre Technique du Bois, No.97,
    1975, pp.67 (Fr.).

Outlines the theory of gluing, describes the characteristics, uses, advantages, and drawbacks of the main types of glues used in the wood industry, discusses types and difficulties in gluing, and considers the special problems that arise in the gluing of wood-mosaic flooring and in gluing aluminium or PVC to wood.

13. Kollmann, F.F.P., Kuenzi, E.W., and Stamm, A.J.
    Principles of wood science and technology: Part II - Wood-based materials.
    Springer-vorlag, Berlin, 1975, pp.703.

The book consists of 6 chapters. The first chapter deals with 'Adhesion and adhesives for wood'.

14. Horioka, K.
    Projects on the durability of adhesion: Part II.
    Nippon Setchaku Kyokai Shi 12, No.2, 1976, p.55-61 (Jap.).

A review on the durability of plywood adhesives tested for a 6-year period.

15. Kozlovskii, A.L.
    Adhesive and bonding.
    New in life, science and technology, Chemistry Series No.6.
    Novoe V Zhisni, Nauki, Tekhnike, Seriya Khimiya,
    No.6, Klei i skleivanie, 1976, pp.64.

16. A.S.T.M.
    Annual book of ASTM standards: Part 22 - Wood adhesives.
    ASTM, Philadelphia, 1977, pp.1042.

2. CARBOHYDRATE MATERIALS

(see also 24 and 73)

2.1 Starch glues

17. Morris, H.H., Drexil, R.J., and Turner, K.L.
    Reaction of fine media-milled starch or protein with a polymer or polymerizable monomer.
    U.S. Pat. 3,891,580 (June 1975).

Grinding aqueous starch or casein slurries containing pigments in the presence of polymers or polymerizable monomers gave extremely stable emulsions useful as adhesives and coatings for paper and wood.

18. Radley, J.A.
    Adhesives from starch and dextrin.
    Indus. Uses of Starch & Its Deriv., 1976, pp.50.

A review paper.

19. Sirota, J., and Mckenne, M.P.
    Cold water-resistant starch-base adhesive containing Styrene-maleic anhydride resin and fixed alkali.
    U.S. Pat. 3,939,108 (1976).

A cold water-resistant adhesive composition comprising a mixture of starch, a styrene maleic anhydride copolymer having a styrene to maleic anhydride ratio of 1:1 to 3:1, a peptizer, water and sufficient alkali to give a pH within the range of 8.0 to 11.0 with at least 20% of the total alkali, on a stoichiometric equivalent basis, of a 100% fixed alkali product, employed in the form of a fixed alkali, said composition containing 4.8 to 20.0 part styrene maleic anhydride per 100 parts starch.

20. Yasui, S., Kusayama, S., and Ohshima, T.
    Wood adhesives.
    Jap. Pat. 7620,939 (Feb. 1976).

Maleated polybutadiene was treated with starch or carboxymethyl starch, and mixed with carboxylated (or uncarboxylated) SBR latex, ZnO or MgO and ethylene glycol diglycidyl ether (I) or glycerol diglycidyl ether to give water-based adhesive imparting water-resistant bonding. For eg: 80 g polybutadiene (mol. wt. 1650) and 20 g maleic anhydride were heated at 200° for 5 hrs under N and then with 25 g starch at 170° for 20 min and treated with 18 g KOH in 500 ml water to give a solution (II). Lauan was laminated using an adhesive from (II) 10; 48% solids carboxylated SBR latex 7; ZnO 1, and (I) 0.1 g by clamping at 120°/7 kg/cm^2 for 5 min to give a laminate with peel strength 36 kg/cm^2 (100% wood failure) and 27 kg/cm^2 (after 4 h in boiling water), compared with 35 and 23, resp. for adhesive containing unreacted starch.

2.3 Sucrose based glues

21. Chang, C.D., and Konomenko, O.K.
    Sucrose-modified phenolic resins as plywood adhesives.
    Adhesives Age, 5, No.7, 1962, p.36-40.

Investigations were carried out on the replacement of a part of phenol in phenol formaldehyde resin with sucrose. The optimal conditions developed were 0.5 mole phenol, 0.13 mole sucrose and 1.13 mole paraform catalysed by sodium hydroxide. The resin contains 33% of sucrose by weight, replacing about one-half of the phenol used in a regular phenolic resin. Methanol is used to adjust the concentration of the resin to about 50%. Plywood panels bonded with the resin had very good glue adhesion strength.

22. Stofko, J.
Bonding of solid lignocellulosic material.
S.Afri. Pat. 7500,551 (Dec. 1975).

Applying an aqueous solution of sucrose (1) starch (II) or wheat flour, and H_2SO_4 to Douglas-fir veneers or shavings and hot-pressing gave plywood or particle board with improved strength properties. Thus, veneers were brushed on one surface with an aqueous solution containing I 25, II 25 and H_2SO_4 1% in the amount approx. 10 g soln/30 cm^2, overlaid, and pressed for 7 min. at 170° and 12 kg/cm^2 to give 3-ply-plywood with 12 kg/cm^2 shear strength.

23. Huang, H.C.
A study on sugar modified melamine resin for water-soluble enamels.
Taiwan Sugar, 23, No.6, 1976, p.239-40.

When sugar-modified melamine resin was substituted for the unmodified resin in alkyd resin-based coating formulations the performance was similar to that of coatings containing unmodified melamine resin.

3. PROTEINOUS MATERIALS

3.1 General

24. Wake, W.C.
Adhesion and formulation of adhesives.
Palmerton Publishing Co. Inc., New York, 1976, pp.325.

Part II of the book contains a chapter on carbohydrates and proteins as adhesives.

3.5 Casein glues

(see also 17 and 83)

25. Kawahara, N., Ishii, K., and Takemoto, M.
Adhesives.
Jap. Pat. 7498,444 (Jan. 1973).

Aqueous adhesive compositions contained 100 parts protein, 5-200 parts epoxy resins and optionally polyvalent metal-hydroxide. For eg: plywood prepared using an adhesive from casein 100, water 250, NaOH 5, $Ca(OH)_2$ 20, EP 828-38 and allylglycidyl ether 2 parts had higher adhesive strength and water resistance than that preparation without EP 828.

26. Gupta, R.C., Chauhan, B.R.S., Tandon, R.C., Tewari, M.C., and Jain, N.C.
Studies on glued laminated constructions: Preliminary studies on the effect of preservatives on bonding of Pinus roxburghii (chir).
Journal of the Timber Development Association of India 20, No.4, 1974, p.9-13.

The effects of treating planks of P.roxburghii with creosote/fuel oil, PCP, borax/$ZnCl_2$ and acid cupric chromate before and after bonding with casein and cold setting UF resin glues on the bond strength were determined. The choice of preservative depends on the glue to be used and on whether the treatment is carried out before or after gluing.

27. Duncan, T.F.
A look at the industrialized housing market and the adhesives used.
Forest Products Journal,25, No.7, 1975, p.7-18.

A literature search and survey was undertaken to determine characteristics of the industrialized housing with emphasis on the type of adhesives used. Adhesives employed in industrialized house production in order of importance are mastic construction adhesives, polyvinyl acetate resin emulsions, contact cements and tile cements. Minor amounts of phenol-resorcinol resins, casein and urea-formaldehyde resins are also used.

28. Miller, D.G., and George, P.
Hot air test of glue bonds in laminated Eastern white spruce.
Canadian Forestry Service Report OPX 105E, 1975, pp.7.

Existing methods of testing bonds in glued-laminated beams are destructive and therefore limited to material cut from ends of the timber. A hot-air test is proposed which could test bond quality nondestructively at any position along the length of a laminated timber. This report describes a limited study to compare the proposed hot-air test with the standard block-shear test. The hot-air test would usually detect weak casein-glue bonds in laminated Eastern white spruce but was not sufficiently stringent to insure detection of bonds which did not beat the shear-strength requirements of CSA standard 0177-1965.

29. Steiner, P.R., and Chow, S.
Low-temperature durability of common wood adhesives.
Forest Products Journal,25, No.8, 1975, p.26-30.

Cyclic exposures of water-saturated Douglas-fir boards laminated with various adhesives under ambient (20°C), moderate-frigid (-12°C), and extreme-frigid (-65°C) conditions, have shown urea-formaldehyde adhesives to have a greater loss in shear strength than urea-melamine-formaldehyde, phenol-formaldehyde, and polyvinyl-acetate-cross-linked adhesives. Boards laminated with casein, but maintained in a dry state when exposed to these three temperatures, showed little shear strength change during cycling. For most adhesives at frigid exposures, shear strength was found to be a better indicator of bond durability than wood failure. Solid wood exhibited little degradation under similar conditions, suggesting the rigidity difference between the lueline and the wood is an important factor invluencing cold temperature durability.

30. Nakatsuka, R., Suzuki, S., and Tanimoto, S.
    Protein based adhesive compositions.
    Jap. Pat. 7502,032 (Jan. 1975).

Aqueous protein dispersions were mixed with epoxy compounds and hexamethylenetetramine (I) as the hardener to give the title compositions. For example 70 parts granular casein was heated 30 min. at 80^{o} in 300 parts 2 % NaOH and stirred with 92.5 parts precipitated $CaCO_3$ and 100 parts of the solution was mixed with 1 part glycerol diglycidyl ether and 0.5 parts I and coated on both sides of a 1.3 mm thick Lauan core, which was placed between 0.65 mm thick panels, prepressed 10 minutes at 10 kg/cm^2 and hot pressed 60 sec at 120^{o} and 10 kg/cm^2 to give laminated panel with tensile shearing strength 17.3 kg/cm^2, compared with 12.7 kg/cm^2 for a panel prepared without I.

31. Nakatsuka, R., Suzuki, S., and Tanimoto, S.
    Protein based adhesive compositions.
    Jap. Pat. 7502,033 (Jan. 1975).

Aqueous protein dispersions consisting of yeast slurries ($>$ 10% solids, $>$70% crude proteins), and alkaline substances were mixed with hydrophilic liquid epoxy resins as the crosslinking agents. For eg.: 100 parts yeast slurry derived from a beer-fermentation tank (15% solids) was stirred 60 min at 80^{o} with 2 parts NaOH and 10 parts casein (80% crude protein, 10% water) and mixed with 25 parts of precipitated $CaCO_3$, and the resulting mixture ($>$ 60 min. pot life at room temperature) was mixed with 15% glycerol diglycidyl ether and coated on both sides of a 1.3 mm thick Lauan core, which was placed between 2.065 mm thick panels and hot pressed for 60 sec. at 120^{o} and 10 kg/cm^2 to give a laminate with adhesive strength (after boiling in water) $>$ 8 kg/cm^2.

32. Kawahara, N., Ishii, K., and Takemoto, M.
    Water-based casein adhesives.
    Jap. Pat. 75,108,333 (Aug. 1975).

Water-based casein adhesives with improved water and heat resistance and useful for laminating wood to wood or other materials contained epoxy resin and polyvalent metal oxide, eg: an adhesive was prepared from casein 100, water 250, NaOH 7,calcium oxide 15, EP 828-38 and allyl glycidyl ether 2 parts.

33. Kawahara, N., Ishii, K., and Takemoto, M.
Water-based casein adhesives.
Jap. Pat. 75,108,334 (Aug 1975).

Water-based casein adhesives with improved water and heat resistance and useful for wood-to-wood, wood-to-asbestos, and wood-to-paper lamination contained epoxy resin and polyvalent metal oxide or hydroxide, eg: an adhesive was prepared from casein 100, water 350, 40% sodium silicate 80, NaOH 2, calcium hydroxide 20, and EP 812-2 parts.

34. Kawahara, N., Ishii, K., and Takemoto, M.
Water-based casein-epoxy adhesives.
Jap. Pat. 75,111,128 (Sept. 1975).

A mixture of casein, calcium hydroxide, borax and optionally sodium phosphate was mixed immediately before application, with 5-200 parts (based on 100 parts casein) of epoxy resin to give water and heat resistant adhesive with good initial strength for wood, metals and plastics, eg: a ball-milled mixture of casein 100, $Ca(OH)_2$ 50 and borax 60 parts was dissolved in 300 parts water and mixed with EP 828-40, 50% SBR latex 60, PhOH and MgO 15 parts to give an adhesive.

35. Kawahara, N., Ishii, K., and Takemoto, M.
Water-based protein-epoxy adhesives.
Jap. Pat. 75,111,129 (Sept. 1975).

Water-based adhesives containing protein (gelatin-casein) and epoxy resin in 100:5-200 ratio were treated with boron trifluoride or tri-ethyl amine and SBR latex, nitrile rubber latex to give adhesives with good water and heat resistance and initial adhesive strength for wood, metal and plastics, eg: a solution from gelatin 100, water 150, $K_2Cr_2O_7$ 0.4, AcOH 15, Epon 812-60, and polyamide hardener 24 parts was mixed with 4 parts boron trifluoride and then 60 parts 50% nitrile rubber latex to give an adhesive.

36. Junichi, K.
Pulverization of colloidal cement additives.
Jap. Pat. 75,139,823 (Nov. 1975).

Colloidal substances such as casein are pulverized with lime, quartz or other rocks and added to cement to increase the adhesive property of the cement, eg: milk casein 3 and quartz sand (No.8) 30 kg were mixed and pulverized for 6 hrs and added to portland cement. The addition of casein increased the binding of the cement to wood materials.

3.10 Other proteinous materials

37. Murayama, S., Nakatsuka, R., Suzuki, S., and Tanimoto, S.
Petroleum yeast protein adhesives for plywood.
Jap. Pat. 74,98,846 (Jan. 1974).

The 2-liq-type thermosetting waterbased adhesives for wood contain dispersions of proteins from petroleum yeast in aqueous alkali and cross-linking liquid epoxides. Thus 100 g of purified dry petroleum yeast cultured in n-paraffin was heated 1 hr in 2.1 aqueous NaOH to give a dispersion. A mixture of the above dispersion 100, polyethylene glycol diglycidyl ether 10, wheat flour 20 and sodium alginate 1 part was applied to veneers and pressed 3 min at 130° and 10 kg/cm^2. The plywood had tensile shear strengths 18.5 (dry) and 9.5 kg/cm^2 (wet), compared with 17.3 and 7.5 respectively, for similar plywood adhered with conventional urea-formaldehyde resin.

4. TANNIN

4.1 Tannins in general

(see also 62)

38. Martin, B.
Energy crisis spurs research in veneer gluing technology.
British Columbia Lumberman, 59, No.5, 1975, p.30-1.

The Western Forest Products Laboratory in Vancouver, Canada, is carrying out research on the adhesives used for plywood. As petroleum prices increase, phenolic products from bark that could be used as plywood adhesives become increasingly desirable. The laboratory has isolated problems in using bark phenolics, but the author does not elaborate on them.

39. Roy, D.C., and Chowdhury, S.
Identification of glue in plywood glue line: Part II.
IPIRI J., 5, No.2, 1975, p.64-6.

Identification of glues containing tannin by microscopic examination of sections stained with $FeCl_3$ and dilute H_2SO_4 is described.

40. Singh, S.P.
A note on tannin formaldehyde adhesives.
Journal of the Timber Development Association of India, 21, No.4, 1975, p.11-7.

The cost of synthetic resins is very high in India, due to the high cost of their constituent chemicals. The condensed tannins which are found abundantly are phenolic in nature and these react with formaldehyde to produce phenol-formaldehyde type of resins, which can be utilized for the manufacture of plywood, particle board, etc. Therefore the ways and means for the utilization of these naturally occurring polyphenols (tannins) as adhesives from waste materials have been suggested.

41. Konishi, M., and Ota, T.
Tannin adhesives for plywood.
Wood Industry, 31, No.4, 1976, p.27-32 (Jap.).

42. Prokhorchuk, T.I., Tsatska, E.M., and Isaeva-Ivanova, L.S.
Furance setting resin from spruce bark.
Vsb. Khim. i Mekh. Pererabotka Drevesiny i Dreves.
Otkhodov L. 2, 1976, p.25-32 (Russ.).

43. Ohta, T., and others.
Adhesives for wood.
Jap. Pat. 76,125,423 (Nov. 1976).

Adhesives were prepared from 30-40% (solids) tannins, 5-25% (based on the tannins) synthetic rubber latexes, and 5-25% (based on the tannins) melamine-formaldehyde copolymer or a similar copolymer. Thus, an adhesive for wood comprised Acacia tannins 100, water 113, NaOH 0.9, coconut powder 13, 97% paraformaldehyde 19.4, SBR 7702-40, and melamine 15 parts.

44. Hemingway, R.W., and Mcgraw, G.W.
Southern pine bark polyflavonoids: structure, reactivity, use in wood adhesives.
Proceedings of TAPPI For. Biol. Wood. Chem.
Conf. 1977, p.261-9.

The structure of flavonoids from southern pine barks, molecular weight distribution of H_2O-soluble tannins, reaction of tannin model compounds with formaldehyde, and adhesives based on formaldehyde-bark alkaline extract reaction products are reviewed.

4.2 Wattle bark tannin

45. Horioka, K., Sugano, E., Katsuzawa, Y., and Hayashida, K.
The synthesis of tannin adhesives and their properties.
USDA Forest Service, Forest Products Laboratory, Madison, Adhesives Symposium, Sept.1975, and IUFRO Working Party on Wood Gluing, 1975, pp.27.

Chemically, wattle bark tannin grown in Japan is similar to commercial wattle tannin from South Africa. Tannin resin adhesives using paraformaldehyde are used in Japan but bond strength must be improved. Thermal degradation of tannin resin adhesives is greater than phenol resin adhesives. Durability of phenol and tannin adhesives is superior to urea and melamine-urea adhesives. Resorcinol-phenol-tannin adhesives are superior to resorcinol-phenol-formaldehyde resin adhesives.

46. Saayman, H.M., and Oatley, J.A.
Wood adhesives from wattle bark extract.
USDA Forest Service, Forest Products Laboratory, Madison. Adhesives Symposium Sept.1975 and IUFRO Working Party on Wood Gluing, 1975, pp.15.

Black wattle (Acacia mearnsii) bark extract contains 70% polyphenolic tannins, used to make a wide range of wood adhesives. Thermosetting unfortified tannin-formaldehyde adhesive is used at 10% of chip mass for weather resistant particle board; 15-20% furnish M.C. is possible without blowing during hot pressing. Waterproof particle board requires 12-14% resin. Neutral pH is used; pressing cycles are as fast as for urea-formaldehyde resin. For interior plywood unfortified tannin-formaldehyde is used; phenol-resorcinol-formaldehyde is added for waterproof bonds. Reactivity is greater than for phenol. So assembly and press times can be reduced. Phenol-fortified shuttering board is made as well as a resorcinol-tannin-formaldehyde cold-setting laminating and finger-jointing adhesive. Future supplies of spray-dried resin adhesives are assured through continued afforestation of black wattle in South Africa.

47. Saayman, H.M.
Wattle tannin adhesives for wood bonding.
USDA Forest Service. Forest Products Laboratory, Madison. Adhesives Symposium, Sept.1975 and IUFRO Working Party on Wood Gluing, 1975, pp.4.

Polyphenolic flavanoid tannins extracted from black wattle (Acacia mearnsii) bark have reactive centres in the para positions of the benzeneoid nucleii. They behave as typical phenols in reactions with formaldehyde, and can be used to make tannin-formaldehyde adhesive resins. Unfortified adhesives for exterior grade particle boards have an expected life span of over 20 years; surface treatment and edge sealing are required for outdoor use. During manufacture, 20% moisture content is possible in particles without blowing the board after hot pressing; 0.5-0.75 inch thick boards can be pressed in 3-5 min. at 180-190°C. Exterior grade plywood requires fortification with phenol, marine grades require phenol and resorcinol. Resorcinol-tannin-formaldehyde resins can be used for cold setting laminating adhesives.

48. Scharfetter, H.
Glulam manufactured with intermediate temperature-setting plywood adhesives.
Forest Products Journal, 25, No.3, 1975, p.30-2.

A substitute for resorcinol-based adhesives used in manufacturing glulam beams was urgently required on account of the acute shortage of resorcinol which arose in South Africa towards the end of 1973, and which is likely to continue indefinitely. A commercial phenolic plywood adhesive and wattle tannin adhesives modified with small quantities of phenol and resorcinol were found to be suitable for this purpose provided the beams were heated during the curing stage. The tannin adhesives were preferred because the temperatures required for curing were lower. It is essential to maintain a sufficiently high relative humidity in curing chambers to prevent the timber from becoming dried out. Facilities for curing at elevated temperatures in laminating plants appear to be economically justified, because the adhesives tested cost much less than conventional laminating adhesives.

49. Okuma, M.
Plywood properties influenced by glue line.
Wood Science and Technology, 10, No.1, 1976, p.57-68.

The effect of the number and the location of the glue lines in the cross section on the bending properties has been studied on plywood bonded with tannin-formaldehyde adhesive. The thickness of glue line has also been investigated. By comparing the theoretical equations with the empirical ones, we can get the thickness of the glue line of wattle tannin adhesive plywood to be 0.15 mm. Young's modulus in bending of the glue line of phenolic resin is calculated to be 219 kg/cm^2 and is larger than that of the glue line of phenolic resin bonded plywood. In relation to the veneer, Young's modulus of the veneer under the condition of plywood assembly seems to be slightly larger than that of the veneer under the free condition.

50. Saayman, H.M., and Oatley, J.A.
Wood adhesives from wattle bark extract.
Forest Products Journal, 26, No.12, 1976, p.27-33.

Condensed flavonoid tannins from the bark extract of Black wattle (<u>Acacia mearnsii</u> Dewild) were used to prepare thermosetting adhesive resins for the production of exterior grade plywood, blockboard and particle board and a cold setting adhesive formulation for finger jointing and lamination of timber. Unfortified tannin-formaldehyde resins were used to produce semi-exterior grade plywood. Phenol- or resorcinol-formaldehyde fortifying resins were incorporated in wattle-base glues for fully exterior grade plywood and construction blockboard. The main benefits derived from these glues were neutral glue lines and faster press cycles. Weather resistant particle boards were produced with an unfortified tannin-formaldehyde formulation at 10 per cent level on wood chip mass while at 12 to 14 per cent level, exterior grade board was manufactured. Copolymerization of tannins and resorcinol with formaldehyde yielded a cold-setting adhesive for lamination of South African *Pinus radiata* timber. This adhesive passed the relevant British and South African Standards for European beechwood.

51. Ohta, T., Araki, K., and Kabe, T.
Adhesive compositions.
Jap. Pat. 7695,439 (Aug.1976).

Adhesives for wood were prepared from mimosa or quebracho tannins and formaldehyde-urea copolymer (I) or a similar copolymer. Thus, 1-5 mols formaldehyde was adjusted to pH 7.8-8 with NaOH, mixed with 1 mol urea, heated at 40° for 30 min. to prepare I (61% solids), and mixed with 50% aqueous tannin in ratio 1:1 to prepare an adhesive.

52. Roy, D.C., Maha, P., and Nag, J.
Tannin adhesives for plywood manufacture: Part III.
IPIRI Journal,7, No.1, 1977, p.1-4.

Deals with the use of mimosa tannin for different types of hot setting adhesives. Seven glue formulations for the manufacture of WWR, CWR, BWP grades of plywood are given with their glue adhesion strengths.

4.4 Quebracho tannin

(see also 51)

4.8 Other tannins

53. Steiner, P.R., and Chow, S.
Some factors influencing the use of Western hemlock bark extract as adhesives.
USDA Forest Service, Forest Products Laboratory, Madison. Adhesives Symposium, Sept.1975, and IUFRO Working Party on Wood Gluing, 1975, pp.25.

Some physico-chemical properties of Western hemlock bark extractives were examined and related to its potential use in wood adhesives. Age of bark and method of extraction affected final adhesive quality. Absorption spectra indicated a marked increase in colour instability of aqueous extract with increasing temperatures at pH over 5.3. Differential thermal analysis (DTA) thermogram and gelation studies showed reactions of extractives with formaldehyde resembled phenol-resorcinol formaldehyde resin especially in terms of exothermic reactions. DTA thermograms showed temperatures over 170°C needed for resin cure 20-30% W/W formaldehyde to bark extract solids necessary for cured resin with maximum softening temperatures of 160°C dry and 180°C wet. Press temperatures of 180°C produced plywood bonds with bark extract-formaldehyde having shear strength and wood failure of 1.17 MPa (170 psi) and 57% after boil-dry-boil tests. Lower press temperatures decreased bond durability.

54. Steiner, P.R., and Chow, S.
Factors influencing Western Hemlock bark extracts used in adhesives.
Information Report, Western Forest Products Laboratory, Canada No.VP-X-153, 1975, pp.25.

The suitability of aqueous extracts of the bark of Tsuga heterophylla for use in adhesives for plywood or particle board was studied. Extracts were obtained by cold pressing the fresh bark or by extraction with water, and their stability was examined. Reactions with formaldehyde were studied by measuring gelation times and by differential thermal analysis. The curing characteristics of the bark extract/formaldehyde resin resembled those of phenol/resorcinol/formaldehyde resins. Exploratory plywood bonding experiments indicated the practical conditions of effective use of the bark extracts.

55. Kulvik, E.
Chestnut wood tannin extract in plywood adhesives.
Adhesives Age,19, No.3, 1976, p.19-21.

Chestnut wood tannin extract, a hydrolyzable tannin, has been used to replace part of the phenol in normal alkaline phenol-formaldehyd plywood adhesives in Malaysia for boil- and weather-proof plywood. The chestnut wood tannin extract in spray-dried powder form contains 70% tannins as polyphenolic compounds and about 22% nontannins. Trials at 20 plywood factories showed satisfactory performance with the chestnut-modified phenol-formaldehyde (PCF) adhesives having about the same properties as unmodified adhesives with respect to viscosity, solids content, acidity, storage life, pot life and glue mixture. Glue spread, assembly time, pre-pressing time, and hot pressing time are the same as for pure unmodified adhesives. The advantages of PCF is reduced as high as the price of the chestnut wood tannin extract. The disadvantage of PCF is higher sensitivity to variations in conditions during plywood manufacture. Results of cyclic boiling and drying tests on meranti plywood manufactured with the modified adhesive are given, along with specific adhesive formulations. Chestnut tannin can replace phenol at a rate of up to 50% with satisfactory results.

56. Kulvik, E.
Chestnut wood tannin extract as cure accelerator for phenol-formaldehyde wood adhesives.
Adhesives Age,20, No.3, 1977, p.33- 4.

5. LIGNIN

5.1 Lignin based adhesives

57. Roffael, E., Rauch, W., and Beyer, S.
Lignin-containing phenolic-formaldehyde resins as adhesives for gluing veneers: Part II - Sulphite waste liquor in combination with phenolic resins.
Holz als Roh- und Werkstoff, 32, No.12, 1974, p.469-72. (Ger.).

The rate of condensation of lignin sulphonates by thermal treatments in an acidic medium and in the presence of phenolic resins can be greatly increased. On the basis of these findings, it was proved that specially prepared lignosulphonates can be used to partially substitute phenolic resins in plywood manufacture. At a pressing temperature of 190°C, about 30% of the phenolic resin used can be substituted by lignin sulphonates without reducing the physical and technological properties of the boards. However, at a pressing temperature of 165°C, the substitution of more than 10% phenolic resins leads to a considerable decrease in the physical and technological properties.

58. Zhadnova, R.S., Sokolova, A.A., and Kochergin, V.M.
Heat-setting adhesive resins from demethylated and tall oil lignins.
Khim. Ispol'Z Lignina, 1974, p.428-33.

Lignin-phenol-formaldehyde resin (I) was prepared in two stages; first modified lignin (II) obtained either by the alkali hydrolysis of the sulphate or the residue from the tall oil manufacture, was condensed with phenol in the presence of H_2SO_4 at 105-110°, then the condensate was reacted with formaldehyde in alkaline solution at 80-100°. (I) had excellent adhesion to wood and it would be used as the binder for particle boards. The optimum (II) phenol-formaldehyde ratio was 30:100:50 weight parts.

59. Yamamoto, Y., Higuchi, K., and Okada, K.
Synthetic resins from wood extracts.
Jap. Pat. 75,121,392 (March 1974).

A phenolic resin useful as an adhesive for wood products was prepared by polymerising phenol and formaldehyde at 80-90° with lignin decomposition products. The lignin decomposition products contained cresol and catechol components and were obtained by exposing wood extractives to an electron beam. The obtained resin had 1.5-2 p viscosity at 30°C.

60. Kilpelainen, H., Forss, K., and Fuhrmann, A.
Lignin-based adhesives for the board industry.
USDA Forest Service, Forest Products Laboratory,
Madison, Adhesives Symposium, Sept.1975, and
IUFRO Working Party on Wood Gluing, 1975 pp.21.

The Finnish Pulp and Paper Research Institute has developed and patented a lignin-based adhesive (Karatex) for plywood and particle board manufacture. High molecular weight lignin derivatives are co-polymerized with phenol-formaldehyde resin. Laboratory test results greatly exceeded American and Finnish Standards for softwood and hardwood plywoods. Press times, temperatures, assembly times, etc., are given with shear strengths and wood failure percentages of typical plywood panels.

61. Shen, K.C.
Acidified spray-dried spent sulfite liquor as binder for exterior waferboard.
Proceedings of Eighth Particle board Symposium, Washington State University, Pullmann, WA.
March 1974, 1975, p.231-46.

Acid-catalysed, spray-dried powder of spent sulfite liquor as binder for exterior waferboard was superior to a previously developed system. The refined process simplified the blending operation, eliminated direct spraying of wafers with acid and reduced the quantity of binder and acid required to achieve acceptable finished waferboard.

62. Glue from pulp waste.
Pulp and Paper Canada, 77, No.2, 1976, p.81.

Recent research efforts to develop adhesives from bark and paper mill wastes were reviewed at a recent symposium at the US Forest Products Laboratory, Madison, Wisconsin. Non-petroleum sources of wood adhesives discussed included tannin extracted from bark and used as a chemical feedstock to produce adhesives, with the bark residues then used for fuel, and lignin wastes from pulp and paper mills. A new chemical bonding technique and a process for recovery of concentrated fodder and adhesives from chemical pulping wastes were discussed. The Finnish Pulp and Paper Research Institute has developed an experimental glue from lignin which can be used in making plywood and particle board. The adhesive has been tested successfully on an industrial scale. Animal feed is also being produced at a prototype plant in Finland, using chemical pulp wastes.

63. Coyle, R.P.
Particle board, hardboard and plywood produced in combination with a lignin sulfonate-phenol formaldehyde glue system.
U.S. Pat. 3,921,072 (1976).

Process for the preparation of an improved glue system for adhering wood particles to each other which comprises preparing a lignin sulfonate formaldehyde prepolymer by heating a solution of a salt of a lignosulfonic acid with an alkali metal hydroxide, thereafter adding a first amount of formaldehyde to form said pre-polymer, thereafter adding phenol to said prepolymer, followed by the addition of a second amount of formaldehyde and heating the resulting mixture to form the glue system.

64. Lee, G.Y., Park, B.K., and Lee, B.G.
Application of lignin: Part 2 - Preparation of lignin resin and its adhesive strength.
Taehan Hwahak Hoechi, 20, No.3, 1976, p.240-3.

Formaldehyde-lignin-phenol copolymer prepared using aqueous NaOH-activated lignin was used as wood adhesive with higher adhesive strength than phenol-formaldehyde resin; optimum conditions were aqueous NaOH concentration 4% and mole ratio in the copolymer 0.3 : 0.0012 : 0.1 at adhesive strength 25 kg/cm^2.

65. Blackmore, K.A.E., and Stout, A.W.
Phenolic adhesives.
U.S. Pat. 3,956,207 (May 1976).

Reacting dried spent sulphite liquor with phenol and formaldehyde gave adhesives for use in manufacture of plywood. Dried sulphite liquor containing 12% phenol and formaldehyde and NaOH (15% of phenol added) was cooked to give 40% mixture (viscosity 1000-1100 cP at 25°) which was spread on Southern pine veneer at 75-80 lb/1000 ft^2 double glue line, and pressed for 6 min. at 300°F and 200 lb/in^2 pressure to give a specimen with 93% wood failure (bottom glue line) for 15 min. stand time.

66. Fross, K.G., and Fuhrmann, A.G.M.W.
Adhesive for use in producing wood products.
Ger. Pat. 2,601,600 (July 1976).

Compounding alkaline solutions of sulfate lignin (I) precipitated from black liquor with formaldehyde-phenol copolymer (II) and additives gave adhesives for use in manufacture of plywood and chipboard. Thus, a mixture (viscosity 1000 cP at 23°) of 37.5% alkaline (I) solution 450, 46% (II) solution 550 and a blend 84 g from wood flour 30, chalk 50 and wheat flour 20 parts was applied on birch veneer at 150 g/m^2 wt, overlaid, prepressed for 7 min. at 7 kg/cm^2, and hot-pressed for 4 min. at 135° and 16 kg/cm^2 to give 3-ply plywood with 32.0 kg/cm^2 dry shearing strength and 91% wood fracture.

67. Johansson, I.
Lignin-based synthetic resins.
Ger. Pat. 2,624,673 (Dec.1976).

Mixtures of sulfate lignin (I) with phenol-formaldehyde solutions containing a curing agent are good adhesives for wood. Thus 10 g purified and air-dried I was mixed with 5 g phenol-formaldehyde solution (prepared by mixing 50 g paraformaldehyde with 100 g molten phenol at 80°) and 0.5 g NH_4Cl, and the mixture was stirred for 1 min. at room temperature to give an adhesive which was used to bond 2 mm thick pine veneer to 10 mm thick chipboard for 5 min. at 150° and 5 kg/cm^2. In delamination tests wood failure was practically 100% and in transverse strength testing chipboard failure occurred at 5.44 kg/cm^2.

68. Yamato, Y., Higuchi, K., Okada, K., and Shibamoto, S.
Lignin-phenol resin adhesives.
Jap. Pat. 76,148,731 (Dec.1976).

Adhesives were prepared from phenol derivatives and lignin obtained from pulp cooling liquor wastes. Thus, a mixture of phenol 50, a 50% kraft paper black liquor 50, 50% NaOH 6, and Na_2O 0.5 parts was heated 15-20 minutes at 60-80°, reacted 6 hours at 75-95° with formaldehyde, diluted with water, and adjusted to pH 11-11.5 with NaOH to give an adhesive containing 40% lignin-phenol resin, which showed good bonding strength towards plywoods.

69. Shen, K.C.
Spent sulfite as binder for particle board.
Adhesives Age, 19, No.2, 1977, p.33-35.

A new process of bonding particle boards with an acidified spent sulfite liquor in either liquid or powdered form in a conventional hot press operation has been developed at the Eastern Forest Products Laboratory, Canada. Press time is similar to that required for similar board made with a phenolic resin. The finished board meets Canadian Standards Association requirements (CSA-0188-68) for exterior grade particle board.

70. Shen, K.C.
Spent sulphite liquor binder for exterior waferboard.
Forest Products Journal, 27, No.5, 1977, p.32-8.

High-strength poplar waferboard can be made with acidified spray-dried spent sulphite liquor (SSL) powder as an adhesive and with a press cycle similar to that used in commercial phenolic waferboard production. In general, laboratory-made SSL waferboards showed aging characteristics similar to those of commercial phenolic waferboard when the conventional accelerated aging treatments were applied. However, these conventional accelerated aging treatments are mainly designed to predict the long-term durability of phenolic bonds in wood composites. The acidic SSL bonds may behave differently from the phenolic bonds in their long-term performance. Further laboratory work has been carried out to determine the effect of acid on long-term durability of SSL-bonded waferboard.

71. Okada, K., Yamamoto, Y., Higuchi, K., and Shibamoto, S.
Powdered lignin-phenol copolymer adhesives.
Jap. Pat. 7708,042 (Jan.1977).

A polymer adhesive for wood was prepared by heating phenol and NaCH at 70-90° and pH 9 for 5-20 minutes, mixing with 100-280% (molar) formalin, heating at 70-95° to molecular weight 200-2000, mixing with 30-60% (molar) lignin (a kraft pulp black liquor containing 30 solids), 50-150% (molar) formalin and NaOH, condensing, concentrating in vacuo, spraying and mixing with 2-10% drying agent.

72. Yamamoto, Y., Koji, H., Okada, K., and Shibamoto, S.
Adhesives for plywood.
Jap. Pat. 7721,305 (Feb.1977).

A formaldehyde-lignin-copolymer adhesive was prepared by mixing phenol with KOH to maintain pH at 12, heating at 80-85° for 10-15 min, mixing with 100-280% (molar) formalin, condensing at 85-95° to mol. wt. 200-3000, mixing with 30-60% (molar) lignin (as a kraft pulp black liquor containing 37% solids), 50-150% (molar) formalin, and KOH, and condensing to molecular weight 300-3000.

73. George, J., Zoolagud, S.S., Narayanaprasad, T.R., Rangaraju, T.S., and Mohandas, K.K.
Partial replacement of phenol in phenol-formaldehyde resin adhesive. Part I - The use of lignocellulosic materials.
Journal of the Indian Academy of Wood Science, 8, No.2, 1977, p.4-12.

Comminuted lignocellulosic materials such as wood, coconut shells and coconut husk after treatment with phenol and/sulphuric acid at boiling water bath temperature can be dispersed in dilute alkali. The dispersion reacts with formaldehyde to give a resin which is suitable for preparing boil proof plywood and boil resistant particle board.

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Experiments with sal wood flour and coconut shell powder show that 50 to 60 per cent of the phenol in PF resin adhesive can be replaced with these materials. The volume of resin obtained is about 2.5 to 3 times the volume of straight PF resin for a given volume of phenol. Replacement of phenol in the plywood glue line is thereby further increased to 60 to 70 per cent. The cost of the resin is estimated to be about 50 per cent of the cost of PF resin calculated on total resin solids.

Coconut shell is particularly suitable as a partial replacement for phenol. The powdered shell may also be dispersed with alkali before (1) condensation with phenol and formaldehyde or (2) being mixed with a high-formaldehyde PF resin to obtain the above economies.

A million tonnes of coconut shells are produced annually in India alone.

6. OTHER GLUES

6.1 Cashewnut shell liquid glues

74. Dhamaney, C.P.
Aniline formaldehyde resins in the field of CNSL based plywood adhesives.
Paintindia, 26, No.8, 1976, p.20.

Aniline and formaldehyde are condensed in the presence of HCl and the resin is mixed with phenol (I) (or xylenol (II)), formaldehyde, cashewnut shell liquid, and an ammonia catalyst and heated at 60-70°. Adhesion tests showed the addition of I and II improved the bonding quality of the resin. Adhesion was also improved by adding a $CuCl_2$ hardener showing that the reaction products are 2-stage resins.

75. Dhamaney, C.P.
Preliminary note on the utilization of oil extracted CNSL shells in the field of CNSL based adhesives.
Paintindia, 26, No.9, 1976, p.19.

HCHO was polymerized with CNSL and oil-extracted, pulverized cashewnut shells (A) to give adhesives; oil-extracted (A) were also used in the manufacture of particle board. Thus 90 parts formaldehyde was polymerized for 45 minutes with 100 parts cashewnut shell liquid and 50 parts A at 60-70° in the presence of HCl polymerization catalyst and $CuCl_2$ hardener to give an adhesive. A typical particle board manufactured from 1 part A and 3 parts sawdust with $CuCl_2$ hardener had bending strength 475.5 PSI.

6.2 Miscellaneous glues

76. Sankaranarayanan, Y.
Adhesives and shellac.
Shellac Export Promotion Council, Calcutta, 1970, pp.70.

Gives formulations of different adhesives using shellac.

77. Kurata, R., and Takahashi, A.
Lecture on latex technology; use of latexes in the field of adhesives.
Nippon Gomu Kyo Kaishi, 47, No.11, 1974, p.735-47.

A review of adhesives for plywood.

78. Shelobanova, V.G., and Riskina, M.A.
Latex adhesive composition.
Prois-vo Shin, Rezinotekhn, i Asbestotekhn.
Izdelii. Nauch.- tekhn. 9, 1976, p.8-9.

79. Eliatamby, D.A., and Nadarajah, M.
Stabilised natural rubber latex adhesive for plywood.
Brit. Pat. 1,455,744 (Nov. 1976).

Formaldehyde stabilized field or centrifuged natural rubber latex containing optional formaldehyde resin is useful as interply adhesive in the manufacture of plywood. Thus, a 55% solids content adhesive at pH 9-10 containing 5% formalin, NaOH, and a 50:50:20 formaldehyde-phenol copolymer stabilized natural rubber-kaolin blend had failing load of 266.3 . and was used to make boil-, moisture- and weather-resistan . mercial plywood.

7. EXTENDERS AND FILLERS

7.1 General

80. Lambuth, A.L.
Adhesives in the plywood industry.
USDA Forest Service, Forest Products Laboratory, Madison, Adhesives Symposium, Sept.1975 and IUFRO Working Party on Wood Gluing, 1975, pp.15.

A general paper giving background information on changes over the last decade in performance requirements for glue lines; changes in plywood manufacture including adhesive application (curtain coaters, sprays and roll spreaders - piece-work crews can still out-perform automated systems on cost performance basis), layup and press conditions for phenolic and urea glues; and glue formulations stressing the roles of various extenders. Extenders are cellulosic (rice and oat hulls, nut shells, tree barks, and wood flours, with new corn cob sources and pulp sludge fines at higher moisture contents); inorganic clays used alone or with cellulosics; starchy extenders to contribute rheological properties related to assembly time and performance tolerances; proteins (blood and soy- generally only urea glues use blood); bark extracts (these are extenders, as only wattle, mangrove or quebracho extracts have adhesive properties); and lignin derivatives (only Finnish Pulp Paper Research Institute product can replace up to 40% of phenolic in a glue). Dispersing agents could be changed - sodium hydroxide can be deleted for phenolic resins and, if ammonia-based catalysts are used, for urea resins as well, then urea added last. Other additives include defoamers, wetting agents, curtain-forming agents, prepressing agents to increase prepress bond strength, glue line identifiers for sales and legal purposes, and viscosity or thixotropic agents.

81. Robertson, J.E., and Robertson, R.R.P.
Review of filler and extender quality evaluation.
Forest Products Journal, 27, No.4, 1977, p.30-8.

Changes in primary extender (filler) for softwood plywood have aroused interest in quality and evaluation of fillers and extenders. Recent technical sessions and reports focussed attention on research and experience with various extenders and fillers. Some alternate products are discussed. Confusing nomenclature is discussed with a proposal to term the lignocellulosic/mineral components 'fillers', and the protein-starch components 'extenders'. Raw material sources and practical quality control procedures are related to the technical economical considerations in making plywood.

7.2 Proteinous materials

82. Minemura, N., Imura, S., Hirata, S., and Sako, M.
Effect of melamine and potato-protein as reinforcing material in the production of urea-treated plywood.
Journal of the Hokkaido Forest Products Research Institute, No.9, 1975, p.5-9 (Jap.).

For the production of Japanese "Type II" plywood with less emission of formaldehyde when a urea-formaldehyde adhesive is used, potato-protein should be mixed with urea during the preparation of the glue, and the veneer used should be of low moisture content.

83. Yamada, H., and Ichikawa, T.
Resorcinol resin adhesives.
Jap. Pat. 7698,740 (August 1976).

Resorcinol resin wood adhesives contained 0.5 - 100 parts of protein, such as casein and defatted soyabean flour, as thickener for improved applicability. For example, a mixture of 100 g 40% aqueous formaldehyde-resorcinol-copolymer and 40 g 30% aqueous casein had viscosity (20°) 1050 cp, compared with 40 for a control not containing casein.

84. Kato, K., Ishitsuka, Y., and Kondo, T.
Adhesives for wood.
Jap. Pat. 76,105,342 (Sept.1976).

Polymerizing a phenol with an aldehyde in the presence of an alkali and a composition containing the resulting polymer, an ethyleneamine, and an aldehyde was useful as an adhesive for manufacture of plywood. Thus a polymer (prepared by polymerizing 1 mol phenol with 1.9 mol HCHO in the presence of NaOH), diethylenetriamine (I) 4, paraformaldehyde (II) 3, soyabean flour 5, and wheat flour 5 parts were mixed. Three lauan veneers were coated (400 g/m^2) with the resulting composition and pressed together at 25° and 10 kg/cm^2 for 3.5 min to give a laminate with a bonding strength of 5.6 kg/cm^2 whereas layer seperation occurred for a laminate obtained with a similar composition without I and II.

7.3 Cereals and starches
(see also 84 and 105)

85. Tsuruta, K., and Nishida, Y.
Plywood with foamed glue.
Jap. Pat. 7506,526 (March 1975).

A process was described for manufacture of plywood by coating the veneers with adhesives such as urea (I) resins, etc., containing foaming agents such as inorganic bicarbonates, and acidic curing agents, such as NH_4Cl and laminating at high temperature and pressure. Thus a paste (viscosity 4.5 p) of 51.1% (I) resin solution (viscosity 1.3 p at 30°) 200, wheat flour 16, soyabean glue 12, 1% aq $NaHCO_3$ 2, and H_2O 40 g was applied on lauan veneers for 5 g/225 cm^2, heated for 30 sec at 80°, and laminated for 15 min at 10 kg/cm^2 pressure to give plywood.

86. Tamura, Y., and Nishina, T.
Decorative plywood laminates.
Jap. Pat. 76,110,008 (Sept. 1976).

A composition containing urea resin and fibrous materials was useful for lamination of plywood with decorative wood. Thus, lauan plywood was coated (15 g/900 cm^2) with a blend containing ML037 (melamine-urea copolymer) 100, wheat flour 20, glass fibres 40 and NH_4Cl 0.5 part, laminated and stored for 8 hr at 80°. No change occurred in storing the resulting laminate joined with a similar composition without glass fibers.

87. Minemura, N., and Imura, S.
Starch waste as an extender of urea-formaldehyde resin adhesive.
Rinsan Shikenjo Geppo, 298, 1976, p.1-3 (Jap.).

Two kinds of starch waste containing rich fiber and skin which were made from potatoes with little or no lime added, were examined for potential use as extender of urea-formaldehyde resin (I) adhesive in plywood production. The adhesive was prepared from I 100, starch waste powder 10-20, water 0-50 and NH_4Cl 1 part at 10-30°. Viscosity of the I adhesives decreased with increasing amounts of water and increasing temperature, and increased with increasing amounts of starch waste powder. The average dry bonding strength of plywoods prepared with the adhesives (spread at 24-30 g/900 cm^2) was 13.0-14.1 kg/cm^2, the average wet bonding strength after soakings in hot and cold water, 10.8-13.0 kg/cm^2.

88. Roy, D.C., Zoolagud, S.S., Naha, P., Chowdhuri, S., and Rangaraju, T.S.
Gelatinized starch blended UF resin adhesives for plywood.
IPIRI Journal,7, No.1, 1977, p.5-9.

It is advantageous to gelatinize starchy extenders such as tapioca, wheat flour and tamarind seed powder before mixing them with urea-formaldehyde resin. The resulting glue formulations give greater coverage than mixes with normal ungelatinised extenders. Plywood made with gelatinized starch extended UF resin conforms to Indian Standards and shows no loss of glue adhesion strength in 18 months of storage at room temperature.

89. Schinabel, A.
Asbestos fiber-extended phenolic adhesives.
Canad. Pat. 100,26,76 (Dec. 1976).

Asbestos fibers were used as viscosity- and thixotropy-control agents for phenolic adhesives for plywood. The fibres should have a kerosene retension of ≯4.25 g/10 g fiber and should be used in amounts of 4-11 parts per 70 parts phenolic resin with sufficient H_2O to produce a flowable mixture. Thus, an adhesive was prepared by mixing (in sequence) H_2O 55, wheat flour 14 phenolic resin 35. 50% NaOH 12, and phenol-formaldehyde copolymer 205 parts. The Brookfield viscosity was 108,000 and 32,350 cp at 4 and 20 rpm, respectively, compared to 15,000 and 7,200 respectively, for a control containing 25 parts lignocellulose instead of asbestos. The adhesive was spread at 40 lb/1000 ft^2 on one side of face and back veneer of southern pine and aged 15-120 minutes before pressing at 300°F for 4 minutes at 200 psi. The product was better than the control in the boiling water test (US Product Standards PSI-66 4.4.3) and in the pressure vacuum test (PSI-66, 4.4.8).

90. Tamura, Y., Fukazawa, A., and Kazushige, T.
Adhesive for plywood manufacture.
Jap. Pat. 7728,915 (March 1977).

A composition containing 100 parts formaldehyde-melamine copolymer (I) and 10-100 parts of a polymer (II) prepared by polymerizing 1 mol PhOH with 2.5-4.0 mols HCHO in the presence of an alkali at pH 8-11 was water-resistant and useful as adhesive for manufacture of plywood. Thus, II (prepared by polymerizing 1 mol PhOH with 2.5 moles HCHO in the presence of NAOH at pH 9 for 1 hour at 80°) 30, I MI 047) 100, wheat flour 25, H_2O 10 and NH_4Cl 0.5 g were mixed. On joining lauan veneers with the resulting mixture, the strength of bonding between the layers was 18.6 kg/cm^2 before and 12.5 kg/cm^2 after boiling in H_2O.

7.4 Bark

91. Inaura, S., Sato, M., Nakamura, A., and Abe, I.
Effects of bark powder on adhesive quality of urea-formaldehyde resin: Part I.
Journal of the Hokkaido Forest Products Research Institute, No.3, 1974, p.9-14.

7.6 Wood flour

92. Tomas, M., and Kosik, M.
Active filler for thermosetting adhesives.
Czech. Pat. 155,568 (Dec. 1974).

Waste lignocellulose, as saw dust, chips, bagasse or corn cobs, containing 40-60% water is treated with steam at 160-170°, and 8-12 atmospheric pressure for 30-120 min., dried at 100-120°, and ground to 0.2 mm grain size to obtain an active filler for thermosetting adhesives (especially phenol-formaldehyde resin adhesives) which takes part in bonding. Thus 200 g of beech sawdust containing 60% H_2O was heated in an autoclave to 165° for 120 min. dried at 110° to 6% humidity and ground.

93. Kubota, M., and Saito, M.
Utilization of sawdust as a filler of plywood adhesive.
Translation, Environment Canada No.OOENV TR-940, 1975, pp.27.
Transl. from Rinsan Shikenjo Geppo, 23, No.7, 1974, p.1-5.

94. Manabe, T., and Yamaguchi, N.
Paste for wall material.
Jap. Pat. 7508.466 (April 1975).

An adhesive paste for plywood having improved workability and fungus resistance was prepared containing sodium carboxymethyl cellulose substitution, degree 0.31, 10, wood flour 100, and water 600 parts. Tetron fibres were also used as fillers for the paste.

7.9 Rice husk

95. Xuan, B., Pollisco, F.S., and Casilla, R.C.
Rice hull powder as a glue filler in plywood manufacture: Part I - Effect on bond quality.
Philippine Lumberman, 20, No.10, 1974, p.26-8.

Shorea squamata plywood panels glued with phenol-formaldehyde resin containing 30-40% rice-hull filler were subjected to dry and boiling shear tests and found to meet the requirements of Philippine standards for Type 1 plywood (for exterior use).

96. Xuan, B., Pollisco, F.S., and Casilla, R.C.
Rice hull powder as a glue filler in plywood manufacture: Part II - Effect on power consumption.
Philippine Lumberman, 21, No.3, 1975, p.16-9.

The power consumed in sawing <u>Shorea squamata</u> plywood panels prepared as described in Part I was not significantly different from that required for panels with coconut shell flour (the standard filler for phenol-formaldehyde adhesives). Results confirm that rice-hull powder is suitable as a filler in plywood for exterior use.

7.10 Other extenders and fillers

97. Katayama, M., Onoe, A., and Tanaka, M.
Fillers for plywood adhesives.
Jap. Pat. 74,126,806 (Dec.1974).

Powders obtained from the waste water from washing rice were used as fillers for adhesives prepared from phenolic resins, urea resins, and urea-melamine resins. Thus, waste water (pH 6.5) from washing rice was mixed with 4 ppm of a flocculating agent and 600 ppm Al polychloride to give a powder (50 mesh), which (32.5 parts dry weight) was mixed with a urea resin solution. Plywood made with UF resin syrup (50% solid) 100, powder obtained from waste water 32.5, water 22.5 and NH_4Cl 1 part gave good adhesion.

98. Katayama, M., Onoe, A., and Tanaka, M.
Peanut shell powder for adhesives.
Jap. Pat. 75,29,661 (March 1975).

Peanut shell powder was used as filler for phenolic, urea or urea-melamine resin adhesive, thus, 100 parts of a urea resin solution (50% resin) was mixed with 20 parts peanut shell powder (50 mesh) and 27 parts water and mixed with 1 part NH_4Cl as hardening agent to give an adhesive, with good bonding properties for the manufacture of plywoods.

99. Tomas, M.
Reducing the release of phenol and formaldehyde by using Fenopreg adhesive and Hycofil filler.
Drevo, 30, No.4, 1975, p.105-6 (Slovak.).

In the context of work hygiene, factory tests were made to compare the release of free phenol and formaldehyde into the air in gluing beech plywood with Fenopreg, a new phenol-formaldehyde adhesive recently developed at the State Forest Products Research Institute at Bratislava and used with lignocellulose filler Hycofil; with two other commonly used adhesives. Results given in tables and graphs, showed that the release of phenol and formaldehyde is 5 times less for Fenopreg than for the other adhesives, and that the sharp rise in this release that is usually observed with increasing moisture content of the wood is almost non-existent in the case of Fenopreg.

100. Lambuth, A.L., and Hearon, W.M.
Thermosetting adhesive compositions extended with cellulosic paper mill sludges.
U.S. Pat. 3,907,728 (Sept. 1975).

Phenol-formaldehyde resin and phenol-resorcinol formaldehyde copolymer adhesives were extended with cellulose pulp and used to manufacture plywood. Thus, 1000 g of PF and 150 g of paper mill sulphite sludge were mixed in water and applied to plywood veneers to give assemblies with average load 173 PSI and 98% failure.

101. Shishido, S., and Hasegawa, K.
Phenolic resin adhesives for plywood.
Jap. Pat. 7533.899 (Nov.1975).

Compositions of 100 parts phenol-formaldehyde resin (I) prepared in the presence of strong base and 7-20 parts beer cake (brewing less) have suitable viscosity and are used as adhesives for plywood. Thus, a composition of 100 parts I and 7 parts beer cake had viscosities 1575 and 2050 cp initially and after 6 hr, resp., and was applied to lauan wood veneers at 30 g/900 cm^2, cold pressed for 20 min. at a pressure of 10 kg/cm^2 and hot pressed for 3 min. at 140° at 10 kg/cm^2 to give plywood having adhesive strengths 25.6 and 20.4 kg/cm^2 before and after immersing 4 hr in boiling water, 20 hr in water at 60°, and 4 hr in boiling water respectively compared with 1650, 3375, 22.0 and 17.5 respectively for a composition of 100 parts I and 10 parts wheat flour.

102. Karpovich, S.., and others.
Use of sulfate lignin for modifying carbamide adhesives.
Teziey Dokl.- Vses. Konf. Khim. Ispol'Z
Lignina, 1975, 1976, p.159-60 (Russ.).

Urea resins modified with alkali lignin (I) as blowing agent are prepared as adhesives for plywood. An adhesive composition containing M 19 26 100, (I) 0.15-0.5 and NH_4Cl 0.5-1.0 weight % increased the delamination strength of the adhesive layer on 24 hour immersion in water.

103. Minami, S., and Yoshizawa, A.
Adhesives containing pulp sludge for plywood.
Jap. Pat. 7700,495 (Jan. 1977).

Pulp sludge was used as an extender to prepare plywood adhesives. Thus, an adhesive comprised Yuroid 301 (urea resin) 100, melamine resin 0.8, pulp sludge 27.5, flour 14.5 and NH_4Cl 0.6 parts.

104. Maejima, T., and Tsuda, M.
Modified urea resin adhesives.
Jap. Pat. 7730,836 (March 1977).

The reaction products of aldehydes with waste liquors from Na_2SO_3 semichemical pulp manufacture were used as extenders for urea resin adhesives. Thus, a mixture of 386 parts semichemical pulp cooking waste (51.8% solids) and 81 parts of 37% formaldehyde was heated 60 minutes at 90-95° to give a reaction mixture (pH 8.88; 49.3% solids). A solution (100 parts) of 3 parts of urea resin and 1 part of the reaction mixture was heated at 80-100° with wheat flour 20, NH_4Cl 0.6 and water 10 parts and adjusted to pH 7-8 with formic acid to give a modified urea resin adhesive which showed dry and wet bonding strengths 17.9 and 12.3 kg/cm^2 respectively, for plywoods, compared with 17.3 and 10.9 respectively for a similar composition without the above reaction product.

105. Maejima, T., and Tsuda, M.
Extenders for urea resin adhesives.
Jap. Pat. 7730,835 (March 1977).

The reaction products of aldehydes with semichemical pulp cooking wastes were used as extenders for urea resin adhesives. Thus, a mixture of 386 parts of semichemical pulp cooking waste (51.8% solids) and 81 parts of 37% formaldehyde was heated for 60 min. at 90-5° to give a reaction mixture (pH 8.88; 49.3% solids). A resin solution (100 parts) of 80% urea resin and 20% of the above reaction mixture was mixed with 20 parts wheat flour and 10.6 parts of NH_4Cl to give an adhesive, which showed dry and wet bonding strength 18.5 and 12.4 kg/cm^2 respectively, for plywoods, compared with 17.3 and 10.9 resp. for urea resin alone.

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