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INDUSTRIAL APPLICATION AND FORMULATION OF SYNTHETIC RESIN ADHESIVES IN THE WOOD BASED PANEL INDUSTRY[1/]

by

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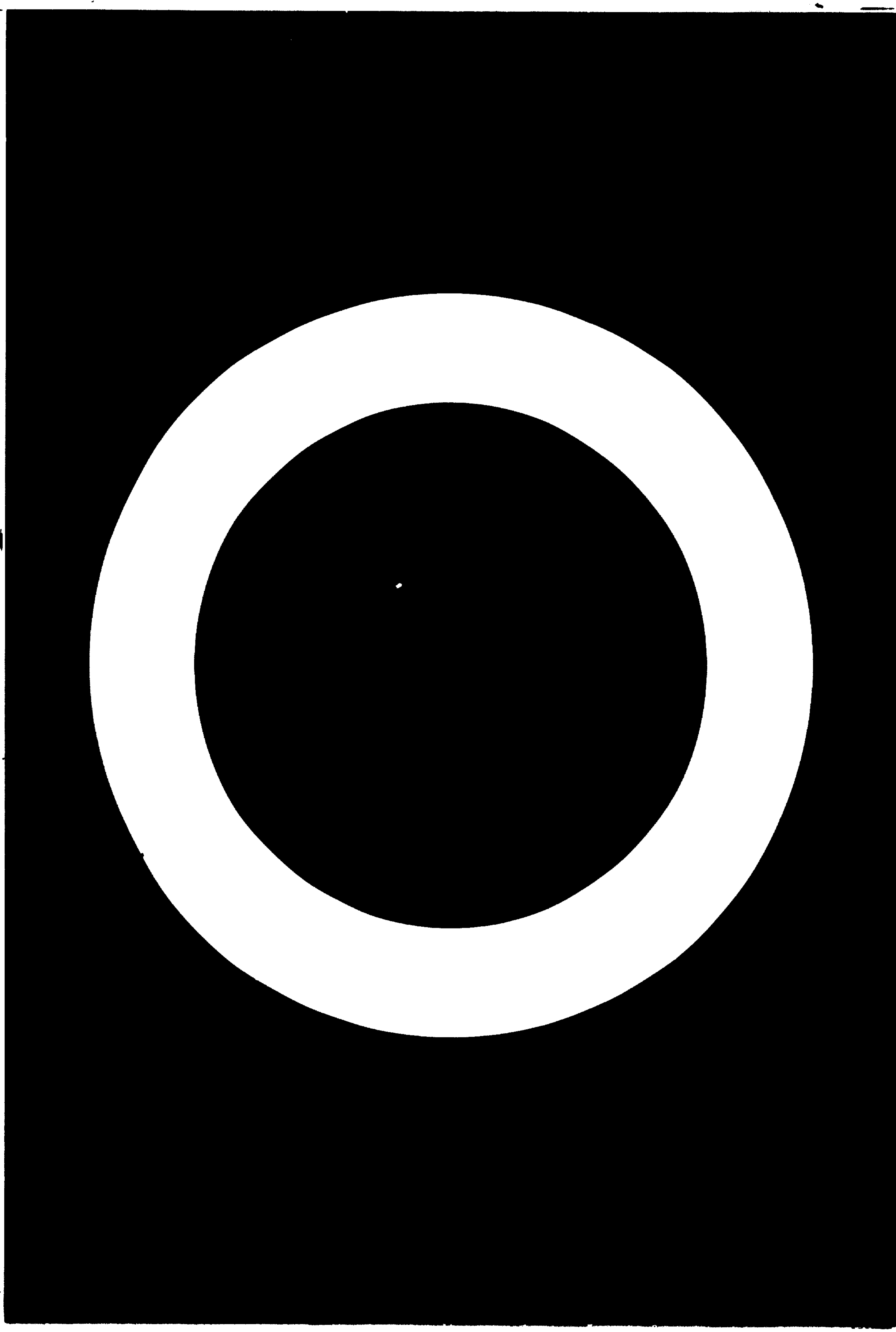

CONTENTS

CONTENTS
(cont.)

1. Introduction

Wood was traditionally joined by mechanical means, as timber is available o. ly in units of limited length, width and thickness. The increasing scarcity and hence cost of timber of good quality and appearance has accelerated the development and application of wood-based sheet materials.

On the other hand one of the most remarkable developments in polymer science is the use of synthetic resin adhesives which are used today in situations which would have been considered impossible some 50 years or so ago. Synthetic adhesives are now recognised engineering materials. Bonding processes have become an established part of production engineering.

With the development of synthetic resin adhesives, gluing offers a neat and efficient method of joining together the separate pieces of wood or of board products such as plywood and particleboard. Gluing has the advantage of making joints less conspicuous; of efficiently transmitting stresses between components, such as in laminated beams and, most importantly, of enabling the width, thickness and length to be increased whilst allowing the bonded article to be further processed as though it were a single piece of wood.

The synthetic organic adhesives we are concerned with here are the classic formaldehyde based thermosetting polymers. All other synthetic binders currently play only an insignificant role in the production of wood-based panels.

A thermosetting adhesive is one that on crosslinking undergoes an irreversible chemical and physical change to become substantially infusible and insoluble. The crosslinking reaction may be initiated by the application of chemicals and/or heat. The most important examples of thermosetting adhesives are Urea - (UF), melamine - (MF), phenol - (PF), and resorcinol-formaldehyde - (RF), formaldehyde being the common raw material for all these resins.

The type of adhesive to select for a particular panel product is, of course, extremely important since amongst other things its properties influence the characteristics and end-usage of the final product. There is no value in using a highly durable polymer if it does not remain attached to the pieces of wood it was intended to bond together. Thus, the most important property of the cured (crosslinked) adhesive is its ability to develop and maintain a good bond strength between the adherends. Consequently, it is the durability of the bond that matters and not just the durability of the adhesive itself.

In the broadest terms the adhesive bonding process embraces the following essential steps :-

1. Preparation of the adhesive mix
2. Applying the adhesive mix
3. Holding the adherends together until the joint has acquired a certain degree of strength.

This paper describes the present use of synthetic resin adhesives in the wood-based panel industries and outlines the preparation of adhesive mixes.

Based on 1971 FAO statistics on the production of wood-based panels and boards the consumption of synthetic resin adhesives is estimated to have been as follows :-

Synthetic resin adhesives consumption in tons net solids

Country	Plywood	Particleboard	Total
World Total	578,500	1,140,400	1,718,900
U.S.A.	258,500	227,400	485,900
Japan	117,500	26,100	143,600
Western Europe	52,000	583,000	635,000

Particleboard and plywood account for most of the synthetic resin adhesive consumption. Urea formaldehyde resins represent the largest part of the resin usage, particularly for particleboard.

2. The present use of synthetic resin adhesives in the wood-based panel industries.

2.1. Adhesives for plywood

2.1.1. Adhesive Durability

Plywood used strictly for internal applications such as furniture needs to have a good dry bond strength but does not necessarily require moisture or water resistance. On the other hand wood-based panel products used externally and exposed to all climates such as in housing require an adhesive capable of withstanding any type of climatic change without fear of breakdown.

Early studies on the performance of formaldehyde based synthetic resin adhesives showed that different types exhibit a wide variation in "durability". Experience with plywood used in naval and aeronautical applications highlighted that UF's were particularly degraded when exposed to moderately severe climates over a short period of time. Further experience suggested that whilst UF based adhesives could be degraded by exposure to weather, MF and PF based adhesives were relatively resistant. Thus, UF plywood exposed to tropical climates was degraded far more quickly than in temperate climates. It was soon recognised that the durability of wood to wood bonds was dependent upon agents such as moisture, heat and mechanical stress. Further laboratory work showed that MF and PF bonded joints could withstand periods of 3 to 6 hours immersion in boiling water without suffering a serious reduction in bond strength. Early specification tests used in Europe and the United States regarded pure MF based adhesives and their modifications (MUF co-condensates or mixtures, mixtures of crystalline melamine with UF resins) as equal to phenol formaldehydes in durability. Practical experience showed however, that this was not true. This led to the development of more severe laboratory tests to separate the more durable phenolics from other adhesives. For British Standards a test involving prolonged immersion in boiling water was adopted.

Results of long term exposure trials have been correlated with the performance in the laboratory of similar joints which have been subjected to immersion in cold, hot or boiling water.

Thus, the types of thermosetting synthetic resin adhesives considered here may conveniently be classified in descending order of durability.

Phenol-formaldehyde (PF) which includes resorcinol formaldehyde (RF) and co-condensates.

Melamine formaldehyde (MF)

Melamine formaldehyde (MF) containing urea formaldehyde (UF) co-reacted or as physical blends.

Urea-formaldehyde (UF) containing crystalline melamine

Urea formaldehyde (UF)

2.1.2. Specification for plywood

In British Standard 1455 August 1972 "Specification for Plywood Manufactured from Tropical Hardwoods" four bonding groups are defined. In ascending order of durability these are INT, MR, BR and WBP. These can be related to chemical groups and environmental conditions as follows :-

Table I

BS Type	Chemical Type	Environment
INT	UF with high proportion of filler	Indoor-not load bearing
MR	UF with filler	Indoor - load bearing
BR	UF upgraded with melamine or MF resin	As for MR but improved outdoor performance though not permanently durable.
WBP	Phenolics (including resorcinols)	Outdoor unprotected

Other plywood standards use cyclic tests involving short periods of immersion in boiling water alternated with soaking in cold water and forced drying of the plywood as in German (DIN) and United States Standards. The table overleaf gives approximate equivalents of various National Standards for plywood :-

Table II

Approximate equivalence of National Standard Test procedures.

Country and Specification Number	Germany DIN 68705	Japan Export plywood Standard	U.K. BS 1455	U.S.A. CS35-63
Durable Category and Chemical Type of Adhesive :				
Most durable : phenolic	Type AW-100	Type I	Type WBP	Type I
MF-UF with up to 40% UF	Type AW-100	Type I	-	Type I
Fairly durable : UF resin with 15-20% melamine added	Type A-100 *	-	Type BR*	-
Good water resistance less resistant to prolonged wetting and drying : UF with some filler	Type 1W 67	Type II	Type MR	Type II
Resistant to cold water for short periods. Heavily extended UF.	Type IF 20	Type III	Type INT	Type III

* A 100 calls for immersion in water at 100° C. for 6 hours, BR only for 3 hours.

In most plywood standards the tests used are to verify the bond quality and to group the types of adhesive used. It is thus important to realise that the test methods are purely comparative. Such accelerated tests cannot be used with confidence to predict the durability of the bond until such time as convincing service records have been collected.

2.1.3. UF plywood adhesives.

Urea formaldehyde resins and their inexpensive extended mixtures have found wide acceptance as adhesives for plywood and have served the adhesive needs of the plywood industry very well.

The preferred UF plywood and veneering resins have a molar ratio of 1 urea to 1.6 - 2.0 formaldehyde. Such resins are available as viscous liquids with a resin solids content of 65-70% which are stable for several months at 20° C. If a resin is required in powder form the water in the liquid resin is evaporated almost entirely by spray drying. Powder resins in general have the advantage of longer storage life i.e. 12 - 18 months and are redissolved just prior to use. UF resins provide a nearly colourless, fast curing glue line that is in general immune to attack by micro-organisms. On a cost-performance basis they have no present equal.

The bonding strength of UF plywood resins can be varied depending on the degree of modification. The addition of fillers and extenders may be accompanied by a reduction in bond strength and in extreme cases, such as tea chest and interior grade plywood, the adhesive formulation may contain more filler than synthetic resin on a weight basis e.g. :-

UF resin powder	100 parts by weight (pbw)
Wheat flour	150 parts by weight (pbw)
Powder hardener	2.5 parts by weight (pbw)
Water	270 parts by weight (pbw)

It is customary to determine under actual factory conditions the most economic adhesive formulation and processing conditions to meet a particular standard of performance. The wood species to be bonded play an important role in this determination as can be seen from the following examples :-

Two UF glue mixes are compared on beech and red Meranti veneer when tested according to the MR and INT requirements of BS 1455.

	Formulation I	Formulation II
UF powder resin	100 p.b.w.	100 p.b.w.
Wheat flour	20 p.b.w.	45 p.b.w.
Powder hardener	2.5 p.b.w.	2.5 p.b.w.
Water	60 p.b.w.	100 p.b.w.

Table III

Bond quality according to the knife test of BS 1455 after INT[1] and MR[2] treatments.

Formulation I	Beech	Red Meranti
INT	7	9
MR	0	7
Formulation II		
INT	2	8
MR	0	6

1 Immersion in water for 16 - 24 hours at 15 ± 5° C.

2 Immersion in water at 67 ± 3° C. for 3 hours

2.1.4. Modified UF plywood adhesives.

On the other hand addition of crystalline melamine or MF resin to UF resin produces a remarkable rise in boiling water resistance. The durability of such modified UF resins is also greatly improved but over long periods they do not compare with phenol formaldehyde. Melamine modified UF glue mixes are almost colourless and they therefore play an important role in the manufacture of decorative plywood with thin sliced veneer faces. This type of plywood is being used extensively for the production of "semi-exterior" flush doors. In general pure melamine formaldehyde adhesives have little use in the manufacture of plywood on account of their cost and in terms of performance they have been replaced by phenol formaldehyde.

2.1.5. PF Plywood adhesives.

The field of truly exterior and marine plywood is dominated by phenol formaldehyde resin. PF resins have high strength properties under all conditions of exposure. Long term weathering tests have shown their ability to withstand the most severe conditions without deterioration. The highest specification for plywood makes the use of PF based adhesives almost mandatory. The most imporant type of PF resins used in plywood bonding are the resols which are usually manufactured with a molar ratio of 1.5 - 2.2 formaldehyde to 1 of phenol. PF plywood resins are strongly alkaline and are available in liquid form of approximately 40 to 50% resin solids concentration and as a spray dried powder product which, like UF powder, is dissolved in water just prior to use. Phenolic resin adhesives of the resol type are dark reddish in colour as is the resultant glue line. Paraformaldehyde is usually used to accelerate the setting when press temperatures of between 110° and 130° C. are used.

2.1.6. Adhesive application characteristics.

Generally speaking, PF plywood resins are more demanding than UF based adhesive formulations in terms of processing conditions. Veneer moisture content and surface quality can be decisive in determining the quality of the resultant plywood. PF plywood adhesives are more sensitive to excessively low or high veneer moisture contents, the preferred moisture content should be between 5 and 9 percent. (For UF based plywood adhesives a veneer moisture content of up to 12% can be tolerated.) In order to obtain a good glue line quality an important requirement amongst others is smoothly peeled veneers giving closely fitting surfaces. PF based adhesives are less capable of bridging veneer surface imperfections than UF adhesives on account of the different types of fillers used (cf. glue formulations). Furthermore, the latitude in permissible assembly times for PF coated veneers is considerably less than for UF. Prepressing of adhesive coated and assembled veneers is now an accepted technique used in plywood manufacture. One of its benefits is the transfer of adhesive from the coated to the uncoated veneer which should result in giving a tight bond prior to heat curing of the bond. UF based plywood adhesives have a greater water holding capability than phenolics which tend to dry out quickly. Therefore the permissible assembly time prior to prepressing is longer for UF's than for phenolics. However, prepressing times ie. the time under pressure, are normally shorter for PF's than for UF's i.e. 3 to 7 minutes for phenolics and 7 - 15 minutes for UF's. The compensation for the longer prepress time for UF's is the much greater assembly time tolerance which UF plywood adhesives exhibit. This permits a considerable degree of latitude in operating conditions. Thus those adhesives having the potential to yield the highest durability are in general the most expensive and most demanding in terms of application.

2.1.7. Costing.

Successful plywood manufacture is based on reconciling the technical demands for a particular grade with glue and manufacturing costs. The relative costs per tonne of adhesive mix of the main types of adhesives are given in the table below :-

Table IV

Relative costs per tonne of adhesive mix

BS 1455 type	Chemical type	Relative cost per 1000 kg. mix
INT	Heavily extended UF	1.0
MR	Extended UF	1.3 - 1.4
BR	Melamine modified UF	1.9 - 2.0
WBP	PF	2.2 - 2.3

The price of an adhesive mix per unit weight is only one factor in glue line costs. Adhesive spread coupled with hot press output are probably the most important factors in cost calculations. Using one tonne of adhesive mix and basing the consumption on 3 ply 6 mm. plywood the following approximate volumes of plywood may be manufactured :-

BS 1455 type	Cubic metres of plywood
INT	29.5
MR	25.0
BR	17.0
WBP	15.0

Considering only the actual pressing times to produce one cubic metre 3 ply. 6 mm. plywood in a hot press 8 x 4 ft. 18 daylights at a press temperature of 115° C. we have :-

BS 1455 type	Time required to produce 1 m^3
INT	7.5 minutes
MR	9.0 minutes
BR	10.5 minutes
WBP	17.0 minutes

From the above it may clearly be seen that pressing time is a very important aspect of total production costs. In this connection it should be pointed out that a well made piece of plywood whether using a durable adhesive or not will exhibit high strength when tested under normal temperato indoor conditions. Thus the use of PF adhesives can only be justified, from the point of view of the user, where severe environmental conditions prevail. There is a general tendency to play safe and use PF's for everything although this must often be tempered by limitations imposed by fabrication conditions and acceptable costs.

2.2. Adhesives for Blockboard *

The foregoing discussions on adhesive durability are also applicable to blockboard although slight physical modifications of the adhesive mix may be needed to accommodate the different surface properties involved.

Polyvinylacetate (PVA_c), a thermoplastic adhesive, is however used to bond the strips which form the core of blockboard. PVA_c adhesives develop strength rapidly at room temperature by loss of moisture. Their temperature and moisture resistance is inferior to those of UF adhesives. By using thermoplastic PVA_c adhesive any misalignment of the core strips is rectified during hot pressing of the outer skins to the core. Blockboard specification tests classify the adhesive bond between veneer skins and the core but totally ignore the glue line between individual strips.

2.3. Adhesives for Fibreboard.

Hardboard or woodfibre board has long been produced using indigenous bonding agents. In order to obtain a higher water resistant board 0.5 - 5.0% (based on the dry weight of the wood particles) of a phenolic resin are added depending on the quality of the desired board. The phenolic adhesive binder is usually added as low alkaline dispersion to the fibres and precipitated onto the fibres through adjustment of pH. Recently a considerable amount of work was carried out in the United States in the development of Medium Density Fibreboard (MDF). This process uses a urea formaldehyde resin with a

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* Laminated board	strips $>$ 7/8"
Blockboard	strips $<$ 7/8" - 1"
Battenboard	battens not wider than 3"

particularly low tack or urea stabilised formaldehyde in the molar ratio of at least 1 to 4. Typical formulations are claimed to be as follows :-

Table V

Adhesive Formulations used in MDF Manufacture

Composition in p.b.w.	Interior grade	Exterior grade
Methylol urea solution (1)	100.0	100.0
Urea	46.0	25.0
Melamine	5.8	35.0
Ammonium sulphate	1.5	1.5
Water	69.9	79.0

(1) "UF - Concentrate 85" or "Stay-Form 60"

It is claimed that MDF commands a substantially higher price over high quality particleboard, because of its superior machinability, coatability, dimensional stability and tight homogeneous edges.

2.4. Adhesives for Particleboard

2.4.1. Adhesive Performance.

Particleboard, like plywood, can be broadly classified according to the type of adhesive (binder) used. German Standard DIN 68763 is divided into three parts, each of which provides special requirements of testing, and the development of physical and mechanical board properties directly related to specific adhesives and end use requirements.

Table VI

DIN Type	Chemical Type	Environment
V20	UF binder	Bonding resistant when used in areas of generally low humidity (bonding not weather resistant).
V70	Melmine (usually MF resin) reinforced urea formaldehyde	Bonding resistant against increased humidity (bonding not weather resistant).
V100	Phenolic or phenol resorcinol binder	Bonding resistant to high humidity (limited weather resistance.)

Clearly the statements concerning adhesive durability made under section 2.1.1. are also applicable to particleboard binders. In a broad sense all foreseeable contingencies of particleboard use are anticipated and catered for. There could however be slight differences in the interpretation of a particular use requirement.

It should be clearly noted that phenolic bonded particleboard is considered not completely weather resistant in contrast to WBP plywood. The usual spread of adhesive in plywood is between 100 and 250 g/m^2 single glue line using an adhesive mix with a resin solids content of between 30 and 50%. This spread is, however, approximately 20 to 25 times that considered economically acceptable for particleboard, although the total surface area of the particles is many times greater than in plywood. However, the absolute amount of resin in particleboard is substantial. Adhesive costs in particleboard in fact may comprise from 20 to 50% of the total production costs; in plywood the costs vary between 7 and 20%. Currently UF bonded particleboard accounts for at least 85% of the world particleboard production and phenolic bonded for less than 10%.

2.4.2. Types of adhesive binders used.

Due primarily to their low costs, versatility and ease of application, urea-formaldehyde binders are the most widely used adhesives in the particleboard industry. UF resins offer excellent properties for bonding wood particles for panels intended for interior applications. The molar ratio of contemporary UF particleboard resins is 1 urea to 1.2 - 1.8 formaldehyde. The lower F/U ratio of particleboard resin in comparison to plywood resins decreases the likelihood of excessive formaldehyde fumes during particleboard production and during use of the panels. UF particleboard resins are available in liquid and powder form and have a lower degree of condensation than plywood resins to provide solubility of the resin in the application stage. The amount of UF binder used in the manufacture of particleboard varies depending on the required board properties but is generally between 8 and 10% resins solids on bone dry wood. The approximate effect of resin content on strength and thickness swelling properties of particleboard is shown below :-

Table VII

Effect of UF Resin Content on Particleboard Properties (12 mm. thick board)

Resin addition on bone dry wood in %	% change in thickness after immersion in water at R.T. for 1 hour.	Transverse tensile strength in kg/cm^2	Modulus of rupture in kg/cm^2
4	20	9	170
6	17	11	185
8	9	13	200
10	7	15	215
12	6	16	210
14	5	18	190

It can be seen that increased resin addition reduces the swelling of the 12 mm. thick board which was immersed in water at room temperature for 1 hour. A corresponding relationship exists for the transverse-tensile strength. However, the modulus of rupture levels off at about 8 - 12% resin addition, and beyond this falls through incipient brittleness.

Thus, in any manufacturing operation in which the board resin content is increased, keeping all other variables constant, a considerable improvement in board properties is obtained. However, resin costs constitute a major production expense in particleboard. Returns in terms of board properties from every unit of resin must therefore be maximised. Melamine formaldehyde is more durable and more expensive than UF. It is not usually used by itself in the production of particleboard. On account of their better moisture and heat resistance MF resins are sometimes used to upgrade UF binders. Replacing between 50 and 60% of the UF binder used in particleboard by MF resin will satisfy the quality test requirements of DIN 68763 grade V100 although the specification calls for the use of phenolics. Thus, a particleboard manufactured using a urea-melamine-formaldehyde type binder is characterised by obtaining boil resistance. This improvement in moisture and heat resistance makes the panels qualify for more severe interior applications. This is, however, not adequate for exposing such boards to the outdoor environment.

Recently a modified urea-melamine-formaldehyde resin containing a small addition of phenol has been introduced as particleboard binder satisfying the test requirement of V100. This phenol modification is claimed to reduce the brittleness of the aminoplasts and allowing swelling and shrinkage stresses to be better accommodated during weathering. However, we should remind ourselves that with resins of other chemical formulations, compliance with certain test requirements does not necessarily indicate equal durability and confirmation by actual long term service trials is required.

Phenolic resins, unlike UF's or MF's, are durable and exhibit resistance to breakdown at higher temperatures and humidities. They are the second most widely used binder in the production of particleboard.

Two different types of phenolics are in use :

1. Resols
2. Novolaks

Usually resols are manufactured with a molar ratio of 1.5 - 2.2 formaldehyde to 1 of phenol using alkalis as catalyst. In novolaks the molar ratio is 0.7 - 0.8 formaldehyde to 1 of phenol using an acidic catalyst. Resols are available as liquids with a solids content of 40 to 50% as well as spray dried powders. Novolaks are used as finely ground powders which are crosslinked using hexamethylene tetramine as formaldehyde donor. Novolaks are mainly used in North America for the manufacture of waferboard e.g. "Aspenite". In this process dried flakes are blended with 4 to 6% of powdered novolak. A similar amount of molten wax is applied to the flakes by spraying. One of the difficulties in this process is to distribute evenly this small quantity of binder over the long thin flakes.

Novolaks require a longer cure-time (press time) than alkaline catalysed resols and are 15 - 20% more expensive than liquid resols on a solids basis. The water resistance (swelling) of waferboard is said to be superior to resol bonded particleboard due to the fact that the novolak does not contain any alkali. Under Canadian climatic conditions this type of board seems to have adequate properties when used in exterior applications. It should be remembered that waferboard competes mainly with phenolic bonded softwood plywood.

Compared with UF resins resols are at a disadvantage in a number of respects including solids content, storage life, hot pressing times, tack characteristics, compatibility with e.g. wax emulsions and cost. Furthermore, they impart colour to the resultant board which is however now considered as a sign of quality.

Continuous research to improve the resol particleboard binders has led to the development of rapid hardeners based on fatty acid amides and others as well as reduction in the alkaline content of the resin. Despite this pressing times are still longer for PF's than for UF's.

The quantity of phenolics used in the particleboard industry remains far behind that of UF.

2.4.3. <u>Binder Application Characteristics</u>

The degree of adhesion between resin coated particles prior to pressing is generally referred to as tack. The degree of tack required by different particleboard manufacturing systems varies very widely. Tack requirements depend, even within the same process, on raw materials, equipment and plant environment (relative humidity). Urea formaldehyde and MF modified UF's can be formulated to give the required degree of tack for given conditions. Phenol formaldehyde resins are less flexible in this respect.

Formaldehyde release is influenced by a combination of factors such as type of resin, type and amount of hardeners and amount of binder used as well as board manufacturing conditions. It should be noted that formaldehyde release cannot be completely eliminated since formaldehyde containing synthetic resins require a molar excess of formaldehyde for the condensation reaction to be brought to completion during hot pressing. However, careful control of all variables can reduce it to an acceptably low level. Where formaldehyde release from finished particleboard is objectionable a formaldehyde-binding coating may be applied. It has been claimed that the amount of formaldehyde released from phenolic particleboard is 10 to 20% of that from UF containing boards.

In order to improve the dimensional stability of phenolic bonded boards it is customary to include a post treatment after hot pressing. In the case of waferboard bales of hot pressed boards are stored for 4 to 6 hours at 90 - 95° C. Resol bonded particleboard also benefits from post treatment, this is achieved by hot stacking overnight immediately after removal from the press. Amino resin bonded particleboards must be cooled after hot pressing since stacking boards at temperatures above 65° C. causes rapid hydrolysis of the binder i.e. lack of resistance to decomposition by heat and humidity and hence loss in board properties.

Many of tomorrow's developments will result from needs now apparent in the plywood and particleboard industry. This industry's dependence on synthetic formaldehyde based resins will continue to grow as there is a need for ever-increasing quantities of building materials to be supplied from somewhat diminishing quantities and quality of forest resources.

3. Formulation of Synthetic Resin Adhesive Mixes

3.1. For Plywood and Blockboard

Although UF, MF and PF resins without any filler/extenders have established themselves as outstanding industrial adhesives for bonding wood chips, flakes and fibres into board products

their use as such in plywood and blockboard manufacture is very rare. In general, operating conditions in plywood and blockboard production are broader than in particleboard and consequently resins are formulated into adhesive mixes using ingredients which supplement and extend the performance of the resins to cover the broader requirements. The first requirement for a strong bond is that the adhesive should "wet" the adherend. The glue line must then remain fluid for the veneers to be positioned but without being totally absorbed by the veneers or flowing out of the joint.
Finally the glue line is hardened without the setting up of excessive shrinkage stresses. Compromises have to be made in order to meet these requirements.
A plywood/blockboard adhesive mix based on one of the synthetic resins mentioned above usually consists of :-

1) a liquid or re-constituted powder resin (powder resin dissolved in water.)
2) a hardener sometimes also referred to as catalyst or accelerator.
3) fillers and/or extenders
4) additional water
5) additives, e.g. prepressing agents, glue line identifiers, wetting agents, preservatives, fire retardants, antifoam agents, curtain forming agents.

The resins have been discussed in detail in the previous chapter. Let us now examine the function of the other ingredients.

3.1.1. Hardeners

The hardener (catalyst or accelerator) promotes the curing of the resin itself. UF, MF resins and blends thereof require acidification in order to cure i.e. to bring the condensation reaction to completion. The hardener can either be an acidic substance or a chemical which is capable of liberating acid when mixed with the resin. Depending on the strength of the acid, or acid forming chemical added, UF resins can be made to cure (set) cold as well as under heat. Pure MF resins will, however, not cure at room temperature but require a glue line temperature of at least 50^{0} C. to develop their full properties. This feature gives UF resins their uniqueness as wood adhesives for many purposes. Cold pressing of plywood and blockboard is now seldom carried out on an industrial scale. The acidic chemicals normally used are : ammonium chloride and ammonium sülphate but many others have been described.

3.1.2. Retarders

In order to achieve a more gradual curing process i.e. a better ratio of usable life to curing time, the hardener may also contain a retarding chemical e.g. hexamethylene tetramine, urea, ammonia or melamine. Resin manufacturers usually also supply suitably formulated hardeners for their resins. They can be in liquid or powder form. It cannot be too strongly emphasised that mixing instructions issued by the adhesive manufacturer should be carefully followed. The resin and hardener components should be mixed in the proportions recommended. The use of an excess of hardener to achieve a supposed faster rate of cure may not only have the reverse effect but could also reduce the efficiency of the resultant adhesive.

3.1.3. <u>Fillers/extenders</u>

Fillers and extenders are terms used rather loosely. A filler is a solid, non-volatile adhesive mix ingredient with little or no paste-forming effect. Fillers are insoluble, finely powdered substances that are dispersed in the resin mainly to reduce glue line cost and to a lesser extent control mix viscosity. Owing to reactivity with acids, pH value, and glue line hardness few mineral products are suitable and hence fillers are usually selected from finely ground nut shells or wood flours of small particle size. In theory fillers being fine particles prevent over-penetration by the resin into the wood (pore stoppers) and hence glue line starvation when pressure is applied on the still fluid glue line. Fillers include the following products :-

1. <u>Inorganic</u>

China clay

Chalk

Attapulgite clay (acicular)
(hydrous magnesium aluminium silicate)

2) Shell flours

Coconut shell

Walnut shell

Olive stone

Pecan shell

3) Wood flours

Softwood

Hardwood

Tree bark flours (Douglas Fir)

4) Other cellulosic fillers

"Furafil" - powdered split oat hulls

Powdered rice husks

This list is by no means complete.

Extenders are non-volatile, paste-forming ingredients containing starch in a natural or degraded state; cereal and leguminous flour extenders also contain protein. Their purpose is two-fold; mainly to improve performance and usually to reduce the cost of the adhesive due to their water retention properties. Starchy, glutinous materials improve spreading and setting behaviour of the adhesive and hold water at the glue line for transfer and flow, resisting the strong absorptive forces of dry veneer. In addition they reduce shrinkage stresses set up during curing of the resin. As the viscosity of, e.g. UF adhesives decreases with increasing temperature, the addition of extenders th t form pastes red ces absorption into the wood and so prevents the formation of poor joints due to starved glue lines and bleeding through thin surface veneers. Extenders may be classified as follows :-

1) <u>Amylaceous</u>

a) cereal flours (wheat, rye)

b) leguminous flours (bean, pea)

c) cold water soluble starches (these are pre-gelatinised starches derived from e.g. tapioca, sorghum, potatoes, rice etc.)

d) native starches (potatoes, maize)

2) <u>Water soluble cellulose derivatives</u>

(methylcellulose, carboxymethyl cellulose)

3) <u>Protein</u>

a) spray dried soluble animal blood

b) soyabean flour

The industrially useful effects of UF resin extensions are achieved mainly by starch and protein. Extenders can confer a cohesiveness to an adhesive mix which becomes more pronounced the higher the degree of extension. This cohesiveness is related to the ability of the extender to retain water. Many problems with prepressing of plywood originate from insufficient cohesiveness of the adhesive mix. Besides giving an increased tackiness, starches and proteins also affect the reactivity of the resin/hardener combination due to their formaldehyde and acid affinity. Testing of extenders is therefore essential to ensure that, whatever reduction in cost of the glue mix may have been achieved, this is not at the expense of the required bond quality. Apart from the resin itself, fillers/extenders used in an adhesive mix do establish the performance limits as an adhesive. Thus, careful selection of the filler/extender combination enhances the performance of the resin itself, and this has contributed to the success of formaldehyde based resins in plywood/blockboard production.

3.1.4. Water

The water in a wood adhesive is the carrier of the colloidally dispersed resin which includes certain hardeners and fillers or extenders. It controls the viscosity of the adhesive mix and with conventional glue spreaders also the glue spread. Porous, cellulose based materials such as wood are wetted out by the water so that the adhesive properties of the resin take effect on the cell walls and good contact is achieved at all attainable points on the surface. Thus, transmission of adhesion is a function of the properties of the solvent or dispersion medium i.e. water and not only of its amount.

Additives have to be compatible with the resin and should preferably neither affect the resin handling characteristics nor the resultant bond quality. This applies particularly to insecticides and fungicides which will be discussed in the next chapter.

3.2. For Particleboard

A suitable binder mix for the manufacture of particleboard may consist of :-

1) a liquid or reconstituted powder resin
2) a hardener
3) wax emulsion
4) additional water
5) additives e.g. preservatives.

3.2.1. Hardeners/buffers

Depending on the particleboard manufacturing conditions and on the acidity of the wood itself a resin may be capable of curing by heat alone, but setting is normally accelerated by the addition of hardener and the application of heat. Hardeners are usually added by the user just prior to resin application. These chemicals are again either acidic substances by themselves or can liberate acids when mixed with the resin. The most widely used components are ammonium chloride and ammonium sulphate as they are inexpensive, convenient to handle and yield a high ratio of working life to cure. To extend the working life of a wood adhesive e.g. UF, it is customary to add a buffer such as ammonium hydroxide or hexamine to slow down the rate of condensation at room temperature. Addition of hardener to the resin is needed as the natural acidity of the wood alone may not be sufficient to obtain an economical curing rate in the hotpress.

3.2.2. Wax emulsions

Emulsions of wax in water may be added to the resin to confer a degree of liquid water repellency upon the particleboard. They are alleged to have a secondary function, namely to provide certain slip characteristics in resin blenders, forming stations and caul plates. Emulsions have to be compatible with the particular resin being used. Compatibility problems encountered with phenolics of high pH have largely been overcome. The amount of wax solids added on oven-dry weight of the woodfurnish varies from plant to plant but is usually in the order of 0.6% for UF's and 1.0% for PF's. The wax normally used is a mixture of solid hydrocarbon paraffins with a melting point range from 55 to 90° C. Such waxes are a by-product of the petroleum distillation process. In unrefined industrial waxes small amounts of impurities in the form of oil are sometimes present. These are believed to give rise to difficulties in subsequent bonding operations e.g. surface veneering of particleboard as well as painting. The most commonly used emulsification system is anionic. The type of emulsifier used depends on the pH of the resin with which the emulsion is to be used, on the required mechanical emulsion stability and on costs. To impart good water repellency to the wood particles it is necessary to keep the amount of emulsifying agent to a minimum and to ensure that the wax is as widely distributed over the particle surface area as possible.

3.2.3. Water

The function of the water is to reduce the viscosity of the binder and to increase the volume of binder mix available for spreading onto the surface of particles. Binder application is one of the most critical operations in particleboard production from the point of view of board quality and production economy. Binder application aims at the greatest possible dispersion of the liquid adhesive with small droplets and distributing it sufficiently uniformly over the surface of the particles. The presence of water is also important in the bonding process itself. The moisture imparts greater mobility of the wood furnish and hence facilitates the pressing operation. Migration of moisture takes place during contact of the resinated chips with the hot press platens. This migration is from the surface towards the centre of the panel resulting in the so-called "steam shock effect" i.e. it enhances heat transfer and accelerates the rate of setting of the binder.

3.2.4. Additives

Additives such as preservatives refer to chemical compounds incorporated into particleboard during the course of board manufacture. Such additions may be divided into two groups namely :-

1) Fungicides and insecticides
2) Fire retardants.

Chemical protection against fungi is required when particleboard is to be used under very humid conditions and against termites in areas where the insects occur and may become a hazard. In 1970 West German regulations required that particleboards used for structural purposes and load bearing be bonded with phenolic resins and protected against the attack by fungi. This has given this aspect of board production considerable impetus. The ideal preservative must not adversely affect particleboard properties, be compatible with the binder and give effective board protection over long periods of time. Costs are also an important consideration. The ideal preservative fulfilling all these requirements has not yet been developed and greater attention is likely to be placed on this work.

Considerable interest is being paid to fire retardants as the use of particleboard products in housing and other types of construction gains momentum. Fire retardants are chemical compounds that are normally added during the course of board manufacture. Ideal fire retardants for particleboard must not only be compatible with the raw materials and board process peculiarities but they should also provide glow and smoke emission retardancy and stop flames from spreading. In many fires the major source of danger to life is created by smoke. Although present fire retardants have not yet been perfected, reasonably acceptable fire retardant particleboard can currently be produced at a cost in terms of money and reduction in desirable board properties such as board hygroscopicity.

4. Problems in Adhesive Technology Arising from use of Wood Preservatives.

Plywood and particleboard bonded with durable adhesives are likely to be used under conditions of high equilibrium moisture content which makes such panels susceptible to fungal attack. Such fungal attack may be controlled by a variety of preservatives e.g. pentachlorophenol, sodium pentachlorophenate, fluorine and copper compounds, mixtures of chlorinated phenols, and other patented compounds.

Finished plywood may be treated with preservatives without adverse effect on the glue line provided that an adhesive with a high degree of durability is used (PF and MF/UF). Penetration of the preservative has been found to be blocked to some extent by glue lines and subsequent re-drying, particularly at high temperatures, could be an obvious disadvantage. Such a post treatment cannot readily be used for particleboard (even when bonded with phenolics) due to the lower dimensional stability of particleboard. Treatment of veneers and

subsequent bonding have been carried out on a limited industrial scale. All preservative treatments interfere to some extent with the gluing properties of wood. The bond strength actually developed depends on the degree to which the surface of the treated wood can be restored to normal i.e. drying off moisture retained after treatment and possibly removing salt deposits that may have been formed.
It is now general practice to add preservatives to the binder mix and rely on preservative penetration from the glue line into the wood during hot pressing. Prime requisites are that the preservative (1) is compatible with the adhesive; (2) does not interfere with adhesion; (3) does not adversely affect board properties; (4) does offer adequate protection of the wood. It is difficult to combine all of these requirements. Few preservatives are compatible with all types of resins thus mix viscosity, pot life and rate of setting of the adhesives can be affected. For example very often substantial quantities of preservative have to be added to the glue mix in order to obtain the correct concentration of preservative based on wood weight. This in turn affects mix viscosity and hence spreadability of the adhesive. To guarantee complete protection of the wood some preservatives are limited for use on veneer with a maximum thickness of 1.5 mm. Recently a preservative manufacturer has claimed success in treating veneer up to 3 mm. but it is not known if this claim is limited to certain wood species. In theory treatment of the wood is based on volatilisation of the preservative during hot pressing and thus loss of the costly, active material is possible. Not all preservatives give adequate protection against the range of fungi and

insects encountered under the diverse usage of panel products.

5. <u>Concluding remark</u>

Many of tomorrow's adhesive developments will result from needs now apparent in the panel industry. We see the ever-increasing availability of more sophisticated methods in polymer science as a means of providing products designed to satisfy specific needs.

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