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07679



United Nations Industrial Development Organization

Distr.
LIMITED

ID/WG.248/7 *
27 October 1977

ENGLISH

Workshop on Adhesives used in the
Wood Processing Industries

Vienna, Austria, 31 October - 4 November 1977

ECONOMIC ASPECTS OF TANNIN EXTRACTS AS
WOOD ADHESIVE BINDERS^{1/}

by

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* Reissued for technical reasons.

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1D.77-7661

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1. INTRODUCTION

The use of synthetic binders for wood panels, be they plywood or particleboard, has enabled these industries to expand notoriously since the Second World War, replacing other wood products which had been manufactured until then, from the ever diminishing supply of large logs. Particleboard in this way has been the major factor in the use of wood from small rapid growing trees and from residues of the wood industry as raw material for wood panels and owes its existence solely to the synthetic binders.

Until that time, most of the binders used for plywood were made from casein and blood proteins, which have been since then rapidly replaced by the urea-formaldehyde and phenol-formaldehyde condensation resins.

It is now that the panel industry, especially in developing countries has shown interest in the use of natural sources for their adhesives, replacing the synthetic resins either fully or partly, because of rising costs of petrochemicals.

Due to the higher consumption by humans and ani-

mals of natural proteins such as those above indicated, and their relative small production increase when compared to their demand, their prices have risen greatly and put them out of the wood binder market, when compared to synthetic resins.

There is, however, one natural product that could be used as a replacement for the resin binders now prevalent and that is tannin extracts from the bark or heartwood of different tree species.

The production of tannin extracts has been mainly directed to the tanning of hides in the past, but as it has been steadily replaced by synthetic tanning agents, mainly for technical reasons, the world demand for this product has diminished and it can be said that the tannin extract industry can offer a surplus to be used as a wood panel resin binder raw material.

Tannin extracts have been widely discussed as potential raw materials for manufacturing wood adhesive binders due to the phenolic nature of their components.

Sufficient literature is available to show that the use of tannins is possible as wood panel binders when compared to phenol, but with a few exceptions, they are not being used commercially to any great extent for the manufacture of wood panels such as plywood and particleboard.

The reason for this could be the present easier availability of synthetic products such as urea and phenol and, possibly, that in the international market the price differential is such that it does not warrant the field evaluation and use of the tannin extracts.

Another reason could lay in that more emphasis has

been put in the use of tannin extracts as the unique component, together with formaldehyde, of the wood adhesive binders than as a partial replacement of the resin solids either in the binder or in the final glue mix. The latter alternatives are now technically possible.

The present trend of the ever diminishing petroleum supply, and consequently higher costs of petrochemicals, will justify us from now on a new look into the use of tannin extracts as wood binders, especially in under-developed countries with no oil resources and no petrochemical industry, but with possibilities of economic plantations of tree species that will furnish tannin extracts, either from bark or from heartwood.

2. TANNIN EXTRACT SOURCES

The major sources for tannin extracts occur in Argentina, South Africa, Brasil and Paraguay, and are obtained from the bark or from the heartwood of several species, amongst which are outstanding the Quebracho (*Schinopsis Lorentzii* and *Schinopsis Balansae*) species abundant in the Chaco region of Argentina and Paraguay, and the Mimosa (Black Wattle) (*Acacia Mollissima*) which has been commercially planted in South Africa and Brasil, with main emphasis in the first named country, with experimental plantations in Kenya.

Other species such as chestnut, in North America and Europe, and certain species of the eucalyptus and mangrove families are also known tannin sources, although the production obtained from chestnut has been reduced during the last two decades in comparison with other sources.

It is also known that polyphenols, such as those found in tannin extracts, suitable to react with formaldehyde, can be found in the bark or heartwood of many species which are

now being left unused or used as fuel supply.

In the case of the Quebracho species, tannin is extracted from the heartwood, where it is heavily abundant, but the drawback being in this instance that it is a slow growing tree, in a low rainfall region, which does not allow for economic reforestation, so the supply will eventually run out. However new regions further to the west of Argentina have been evaluated and it has been found that at the present rate of consumption there is enough supply to last for another 80 years of quebracho tannin extract, at the present rate of consumption.

Quite to the contrary, from the Mimosa (Wattle) species, and other similar sources, the tannin is extracted from the bark, so the harvest can be obtained in a relatively short period of time (10 to 12 years) from planting, when compared to Quebracho extract, which is calculated at over 100 years.

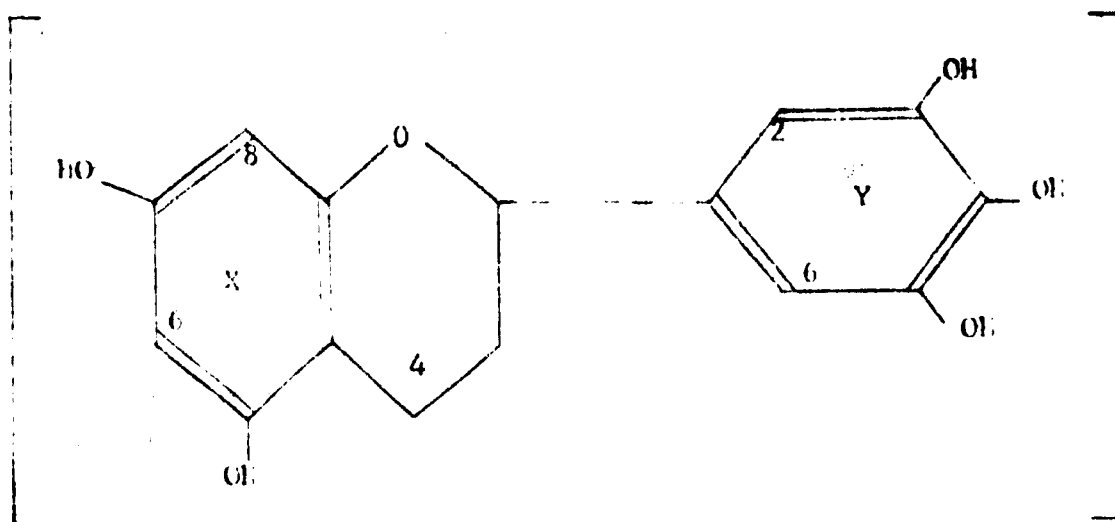
It is perhaps from this mimosa source that tannin extracts can continue to be available, if plantations are made in those countries, where conditions are most suited for economical plantations. If these countries also have extensive timberland, the tannin extract thus obtained could not only be exported but also used locally as a wood binder raw material.

3. CHEMICAL NATURE OF TANNIN

Tannin extracts are natural occurring polyphenols containing reactive points which may react with aldehydes, formaldehyde being the most common, to form thermosetting insoluble products, in a similar manner to phenol and resorcinol, and which, due to their tensile strength properties, are suitable for wood bonding.

All tannin polyphenols in general contain resorcinol nuclei and therefore rapid reaction occurs with formaldehyde in solution, in the presence of small amounts of sodium hydroxide, through its attack of the 6 and 8 positions of the resorcinol-type X rings.

The basic 15- carbon molecule structure is the following, according to several studies made in the past twenty years.-



3-9 MONOMERS

Basically the tannin molecule is formed by a resorcinic nucleus X and a catechinic nucleus Y, united by a pyranic heterocyclic structure. In this structure, positions 6 and 8 are very reactive, and possibly also position 4 of the pyranic ring. Of lesser importance chemically in practice would be the reactivity of the 2 and 6 positions of the catechinic nucleus.

The above mentioned structure corresponds to the

Quebracho tannin extract, while in the Mimosa extract the catechinic ring is replaced by a pyrogalllic nuclei. It is interesting to note, however that, at least for Quebracho, the dimers and trimers of the above described 15- Carbon structure, constitute about 30% of the total product, the precise nature of the remainder not being exactly known.

These basic molecules, through enzymatic action, condense into polymers, mainly trimers and tetramers, mixture of which constitute the commercial grades of tannin extracts, which are now used mainly for hide tanning and water flocculation.

The polyphenols, having a great amount of reactive resorcinic points, react very rapidly with formaldehyde forming methylene links between the macromolecules to produce a resin type polymer which needs a relatively small amount of formaldehyde to set into an infusible solid. This small amount of formaldehyde may be supplied by the direct addition of formaldehyde, as formalin or paraformaldehyde, to the tannin solution and it can also be supplied by the free formaldehyde present in a phenol-formaldehyde resin, or by the reactive methylene groups of the methylol-phenol molecule, thereby forming a combined product.

It must also be taken into account that during extraction at high temperatures or in alkaline media, a certain amount of lignin is taken out together with the tannin. This side product also reacts readily with formaldehyde, and its varying amounts present in the extract will no doubt affect the condensation process of the tannin with formaldehyde, and the cure characteristic and efficiency of the final resin binder.

Tannins are soluble in hot water and can thus be

easily extracted by the action of steam or hot water immersion of the ground bark or heartwood chips. The extracted tannin solution can either be concentrated and cooled to obtain the extract in block form, or it can be spray-dried to have it in powder form.

The extract so obtained is only partially soluble in cold water, and if a fully cold water soluble product is desired, the primary solution is treated with sodium sulphite or bisulphite, thereby introducing sulphite radicals in the 6 and 8 positions of the resorcinic rings of the basic molecules, which enhances the solubility of the product.

The above process is basically that used for the extraction of tannins from Quebracho in Argentina and Paraguay, bark extracts are obtained in other countries in a similar manner.

The choice of either using the hot water soluble (also called ordinary) or the cold water soluble (also called sulphited) for binder manufacture will depend on the way the binder is produced. Being the ordinary grade more reactive, it is preferable to use the sulphited grade when reacting directly with formaldehyde, due to the partial blocking of the reactive points of its molecule with the sulphite radicals. When co-reacting tannin with a highly condensed or a formaldehyde deficient phenolic resin, it is indicated that the ordinary grade be used, and/or an addition of formaldehyde be made.

Regarding solubility of the Quebracho tannin extract, it can be increased very noticeably by raising the pH of the dispersion to about 8 to 9, which means that it can be thoroughly mixed with the high alkaline resole phenolic resins which are normally used for wood binding.

The Quebracho tannin industry in Argentina has prepared a special type of tannin extract with a pH of 8.5 that is readily soluble, as possible raw material for the wood binder market. This type of product, of the ordinary grade, appears to form high tensile strength bonds when applied at that pH level.

Tannin solutions, especially using ordinary grade Quebracho, tend to be high in viscosity, which would be a disadvantage when manufacturing resins, but it has been noticed that the presence of phenol, methanol, urea or acetone, which most certainly dissociate spatial structures united by hydrogen bonding, will drastically reduce the viscosity of the solution, as shown as follows.-

3.1- Variation of solution viscosity with quebracho extract concentration (ordinary grade)

<u>Extract content</u>	<u>Viscosity (cps)</u>
35%	1000
40%	2400
43%	6000
47%	17000

3.2.- Effect of phenol on the viscosity of a 47% solution

<u>Phenol (%)</u>	<u>Viscosity (cps)(25°C.)</u>
0	14000
2,5	4800
5,0	2300
10,0	1000

On the other hand, the solutions of sulphite

grade Quebracho present very low viscosities, which enhance its possibilities as raw material for resin binders, as follows.-

3.3.- Variation of solution viscosity with quebracho extract concentration (sulphite grade)

<u>Extract content</u>	<u>Viscosity (cps)</u>
36%	28
40%	74
45%	284
48%	588

4. MANUFACTURE OF BINDER RESINS

Based on the inherent chemical properties of tannins especially of Quebracho and their affinity with formaldehyde, binder resins for the wood industry can be manufactured by these methods, as follows.-

- Direct condensation reaction with formaldehyde.
- Co-condensation of tannin and phenol with formaldehyde.
- Post addition of tannin to a phenol-formaldehyde resin during its manufacture.
- Addition of tannin to a phenol-formaldehyde glue mix during the wood panel production.

A brief outline of each is given as follows.-

4.1 . Direct condensation reaction with formaldehyde

Due to the high reactivity of the resorcinic nuclei

this reaction is very rapid and gives the resin a very limited shelf life. Basically it can be prepared as follows.-

Tannin	100
Water	100
Formaldehyde (para)	5/9

The tannin, preferably of the sulphite grade is dissolved in water to a 50% solution, and sufficient sodium hydroxide is added to raise the pH to 8, so as to reduce viscosity.

The formaldehyde is added as a slightly alkaline solution of paratormaldehyde or it can be dissolved straight into the resin solution provided it is in powder form.

Due to the natural origin of the tannins, and to the varying amounts of lignin present, resin binders of different reactivities and shelf-lives will result, even if their manufacturing conditions are strictly controlled.

These variations will make it very hard for the panel manufacturer to use the resins as they will either become highly viscous before application or will tend to precure on the wood, be it either during plywood or particleboard production. This problem is greatly increased if the untreated or ordinary grade of tannin is used.

As far as it is known, many field tests have been carried out in the plywood and particleboard industries which, with a few notable exceptions, have been negative when using the above system.

In order to reduce the reactivity variations, and increase the physical properties of the bond, a resorcinal resin

can be added to the above mentioned formula in the proportion of about 20 parts per 100 parts of tannin extract.

Unfortunately the cost of the resorcinol resins is very high, and their availability is not of prime order, so economically such a mix would price itself out when compared to an average phenol-formaldehyde resin.

The reactivity of this mix is highly dependent on its pH when being used, as too high a level would shorten drastically its shelf-life while if the pH is below 7 the pressing cycles would be too long.

Paraformaldehyde added to the mix has to be of the slow release type so that the reaction does not take place too rapidly. The availability of paraformaldehyde in the world market is not marked, its price being much higher than a 37% formaldehyde solution, on an equal solids basis.

4:2 Co-condensation of tannin and phenol with formaldehyde.

In any basic formulation for a phenol-formaldehyde resin binder for wood, phenol is reacted with formaldehyde, in the presence of varying amounts of caustic soda, followed by a condensation process to increase molecular weight and viscosity, and attain the right degree of reactivity.

It has been found that in this process upto 50% of the phenol binder can be replaced by Quebracho tannin extract, with satisfactory results both for plywood and particleboard manufacture.

To obtain a relatively stable product it is recommended that the sulphited or cold water soluble grade be used. A higher proportion of tannin is not feasible as the reactivity and

shelf-life of the resin tends to become uncontrollable, in a similar way as described in Point A above, thus making it unsafe for the end user.

The water resistant and boil proof properties of the resulting panels tend to be reduced somewhat with increasing tannin content upto 50% phenol replacement but do comply with existing specifications. A higher degree of replacement will not be conducive to satisfactory end-products.

4.3 Post addition of tannin to a phenol-formaldehyde resin during its manufacture.

Once the phenol-formaldehyde resin is fully condensed as described in point B above, it is feasible to make a post addition of tannin to the resin solution which, by being highly alkaline, will readily dissolve the tannin at intermediate temperature followed by quick cooling.

The ordinary or hot water soluble grade of tannin can be used due to the insufficient presence of free formaldehyde although the use of the sulphite grade is safer, this process, less critical to follow than that the resins described in the preceding sections, will result in a product of lower reactivity but with a shelf life similar to the original phenol-formaldehyde resin, if not longer.

Given a longer cure time a higher press temperatures, the resulting bonds will meet most of the prevailing specifications, for plywood and particleboard manufacture.

4.4. Addition of tannin to a phenol-formaldehyde glue mix during wood panel production

In this case the tannin extract may be added during the glue-mix preparation at the plywood or particleboard mill, its role being that of an active extender which reacts with the original phenol resin during hot-pressing.

This constitutes the most direct use of tannin as a partial replacement for phenol, with practically no hazards involved as to bond performance, but is applicable only to plywood manufacture, provided the appropriate glue mix and pressing conditions is used.

5. APPLICATION

The different mixes prepared as described in the previous chapter can be applied to the particleboard and plywood industries as follows.-

5.1 . Particleboard

It is by far recommended that a co-reacted resin of phenol and tannin be used, as the method of application and results obtained thereof do not differ in any significant way to the normal process using the straight phenol-formaldehyde resins commonly used for this purpose.

A normal phenol-tannin-formaldehyde resin binder for the manufacture of particleboard would show the following general properties.-

Solids content (135°C)	44-46%
Viscosity (25°C.)	40-70 cps.
pH (25°C.)	11-12
Specific gravity (25/25°C.)	1,20-1,22
Shelf life (20°C.)	30 days

By shelf life it is understood that at the end of the indicated time lapse, the viscosity of the resin binder will be such that it will permit its normal application. The liquid life is of course longer.

A resin of this type is being used industrially in the following conditions.-

Type of equipment	Multi-platen
Type of board	Three layered
Wood furnish	Poplar/Willow
Board thickness	8 to 22 mm.
Board density	0,68-0,72
Press temperature	170-175°C.
Press cycle	0,5 mins/mm
<u>Resin solids (1)</u>	

Surface layer	10-12%
Core layer	8-10%

(1) The resin solids level will of course depend on the type of furnish being used. In this case it is wood from rapid growing trees, which is highly water absorbent. Wood furnish with a closer cell structure or rosin containing would of course need less resin solids to obtain good bonds.

Board properties

Modulus of Rupture (MOR)	240-280 Kg/cm ²
Internal Bond (IB)	5-8 Kg/cm ²
Thickness swell	
Cold water (2 hrs)	5-12%
Boil test (2 hrs)	10-22%
Internal Bond (IB) (2 hrs boil)	2-4 Kg/cm ²

Production runs made at the same particleboard plants with straight phenol-formaldehyde resins under similar conditions showed results comparable to the above.

As mentioned previously the use of a direct condensation resin binder of tannin with formaldehyde has not been successful in general on an industrial scale, while the use of phenol-formaldehyde resin with a post addition of tannin tends to result in long press times. Perhaps the adequate choice of the proper grade of tannin extract, be it of mimosa or quebracho origin, would be conducive to good results with this type of binder.

Because of handling problems at the large particleboard mills, it is not advisable to mix the phenol-formaldehyde resin with the powdered tannin extract at the point of usage. In general and because of the high volumens involved, the mills prefer to handle liquid products which can be easily moved, mixed and applied.

The tannin extract so involved would apply itself only to the manufacture of particleboards for exterior use, as the cost of a straight urea-formaldehyde resin, at equal solids content, would be much lower, as can be seen in the economic analysis detailed further on in this study.

5.2. PLYWOOD

In this industry, when manufacturing exterior grade panels, it is also advisable to use phenol-tannin co-reacted resins, as results can be considered satisfactory, and comparable to straight phenol-formaldehyde resins.

A binder of this type with 50% phenol substitution has been applied according to the following conditions.-

Glue mix

Resin binder (PTF)	100
Wheat flour	20
Wood flour	5
Water	25
37% Formalin	2,5

Conditions

Wood	Paraná pine
Wood humidity	6 - 8%
Glue spread	200 grs/sq.mt.
Press temperature	120°C.
Press time	1 minute/mm thickness
Pressure	10 Kg/sq. cm.

Plywood properties

Dry strength	90-120 Kg/sq.cm.
Wood failure	90-100%
Wet strength (12 hour boil)	60-70 Kg/sq.cm.
Wood failure	40-70 %

As with particleboard manufacture it is not advisable to use resin binders prepared by direct condensation of tannin extract with formaldehyde, because of the high reactivity of the resin thus obtained, which in the prevailing conditions of plywood mills, especially in warm climates, would cause extensive precure if the operation is not supervised very strictly.

Pertaining literature indicates that glue-mix formulations could be developed from the following recipes, provided the above points are taken into account when using same.-

	<u>Ordinary</u>	<u>Sulphited</u>
Quebracho tannin	100	100

Water	140-150	105-115
Caustic soda	1 - 4	1 - 4
Wood flour	15-20	15-20
Paraformaldehyde	5 - 9	5 - 9

The preparation of the above formulations have short working lives, which are highly dependent on the level of caustic added, and the prevailing room temperature.

There is considerable experience in some countries in the use of either the ordinary or the sulphited grades of tannin, especially of Quebracho origin, as an extender for the phenol-formaldehyde glue mix. In this case the tannin replaces only about 5% of the liquid 40% phenol-formaldehyde resin, or say, the equivalent to 12% of the phenol-formaldehyde resin solids. In some cases, if the original resin is highly condensed and therefore with a low free-formaldehyde level, a 0,5% addition of paraformaldehyde or 1,5% addition of 37% formaldehyde solution is made to the glue mix.

In this case a typical glue mix formula would be the following.-

PF resin	100
Quebracho (sulphite)	5
Calcium carbonate	4
Wood flour	3
Paraformaldehyde	0,5
Water	5 - 10

Paraformaldehyde could be replaced by the equivalent amount of a 37% formaldehyde solution.

This glue mix is spread at 300-320 g/ sq. cm. of

double glue line, on birch and the veneers laid up for 10 minutes and then pressed at 125°C. for the required cycle according to the number of plies.

The addition of the Quebracho tannin not only reduces the amount of phenol-formaldehyde resin being used, but also increases the mix's cure speed. This last advantage is enhanced if the ordinary grade of Quebracho tannin extract is used or, better still, if the high pH version of the extract is used. In this case a typical glue mix recipe would be the following.-

PF resin	100
Quebracho (pH 8,5)	4
Wood flour	4
Calcium carbonate	2,5
Wheat flour	2,5
Paraformaldehyde (1)	0,4
Water	6 - 10

(1) Can be replaced by 1 part of a 37% formaldehyde solution.

The viscosity of this mix is very stable, rising from about 350 cps. to 600 cps. in about 24 hours. It is reported that glue mixes such as above are now being extensively used in Finland and Russia mainly with birch-wood panels.

6. TANNIN AS REPLACEMENT FOR OTHER WOOD BINDERS

Until now this paper has dealt with the replacement, either wholly or partially, of phenol-formaldehyde binder resins by tannins extracts due to the latter's phenolic nature. Other binders normally used are the following.-

6.1 UREA-FORMALDEHYDE RESINS.- The urea-formaldehyde binder resins are used for interior purposes and their cost on an

equal solids basis is at such level that it would not permit its replacement by tannin at their present international market level.

There have been some attempts in a tannin producing country to manufacture particleboard with a direct condensation binder of tannin and 37% formaldehyde solution, but due to the short pot-lives and erratic reactivities, as described earlier on, this project had to be abandoned, although economically it seemed justified at the moment.

6.2 RESORCINOL-FORMALDEHYDE RESINS.- The resorcinol-formaldehyde binder resins find a ready but small market in the wood boat-building and laminated beams industry as a cold setting glue. Although economically tannin can replace resorcinol as raw material due to the latter's high cost, this resin's small volume sales and the rather erratic properties of the tannin formaldehyde binder, would not justify the change from an excellent, time proven adhesive, though expensive, such as the resorcinol-formaldehyde resin glues.

7. AVAILABILITY OF TANNINS

As shown in the following pages, the world demand for tannins which had been steadily on the rise since the turn of the century till 1950, has drastically been reduced since the advent of synthetic tanning agents, especially those based on chromium salts, with which light coloured leathers can be obtained.

This reduction of the demand has permitted the tannin industry to make available for other end uses a volume, which at this moment and based on past production figures, can be estimated at 60.000 to 120.000 metric tons per year, without taking into account new plantations or added extractions facilities.

Should mimosa plantations be enlarged according to

7.1 WORLD DEMAND

FOR TANNIN EXTRACTS (1)

<u>YEAR</u>	<u>DEMAND</u> <u>MT</u>	<u>RELATIVE DEMAND (2)</u> <u>%</u>
1940	357.540	100
1945	409.022	114
1950	496.516	139
1955	403.417	113
1960	366.472	102
1965	336.828	94
1970	265.043	74
1974	257.619	72
1975	217.134	61
1976	252.538	71

(1) Source - Argentine - Paraguayan Quebracho Extracts Chamber

(2) Base 1940 - 100

WORLD DEMAND

FOR TANNIN EXTRACTS

BY SOURCE (1)

<u>YEAR</u>	<u>MIMOSA</u> <u>MT</u>	<u>CHESTNUT</u> <u>MT</u>	<u>QUEBRACHO</u> <u>MT</u>	<u>TOTAL</u> <u>MT</u>
1940	105.530	78.691	173.319	357.540
1945	109.496	22.298	277.228	409.022
1950	140.111	82.247	274.158	496.516
1955	139.455	87.468	176.494	403.417
1960	126.103	72.939	167.430	366.472
1965	126.152	57.565	153.111	336.828
1970	110.075	49.722	105.246	265.043
1974	106.789	46.023	104.807	257.619
1975	91.714	40.634	84.786	217.134
1976	109.129	39.271	104.138	252.538

(1) Source - Argentine - Paraguayan Quebracho Extract Chamber

7.2 PRODUCTION OF
QUEBRACHO TANNIN EXTRACTS (1)

<u>YEAR</u>	<u>ARGENTINA</u>	<u>PARAGUAY</u>	<u>TOTAL</u>
1940	141.000	31.810	172.810
1945	241.909	29.508	271.417
1950	157.920	31.410	189.330
1955	186.694	33.925	220.619
1960	126.349	30.396	156.745
1965	108.396	29.322	137.718
1970	92.130	15.036	107.166
1974	92.560	6.022	98.582
1975	69.355	13.329	82.684
1976	92.335	17.904	110.239

(1) Source - Argentine - Paraguayan Quebracho Extract Chamber

the new demand created by phenol-tannin-formaldehyde resins, a steady stream of tannin extract would be made available. As such plantations are hard to develop because of the time consumed and heavy investment involved, the increased demand could meanwhile be met by the Quebracho tannin industry in Argentina.

The demand for mimosa extract has increased in recent years, at the expense of quebracho and chestnut tannins, while it is interesting to note that Brazil has become an active producer of mimosa extract in the past 15 years, an example that could be followed by other countries with similar climates.

Regarding the future, it is said that for leather tanning, each product, namely, natural and synthetic tanning agents, has now reached its respective maximum market-share and each will not encroach on the other as it has been in the past. The reason for this is that chromite leathers, although light in colour, have not the toughness of the natural tanned leather, each type of leather having now its market well defined. This can also be inferred by the world demand of natural tannin extract which has more or less remained stable for the last 6 years after a steady drop since 1939.

Due to the restricted offer of hides caused by the slowly increasing cattle herd in the world, a sudden upturn of the world demand for natural tannins is not envisaged at the moment so that the surplus available for binder resins would not be seriously affected.

There is nevertheless one factor that might alter this balance between both tanning agents, and that is the growing scarcity of chrome ore, caused in a way by the relative economic instability at present of the producing countries although this situation is expected to be transient. If present conditions,

which at this moment are just beginning to be felt, should continue, an increase in the demand of natural tanning agents. would occur to the detriment of the present surplus available for the wood industry.

8. ECONOMIC SITUATION.

The average international prices for the different raw materials used for binder resins, are approximately the following, at FOB points.-

Paraformaldehyde	U\$S 700.- per MTon.
37% Formaldehyde	U\$S 120.- per MTon.
Phenol USP	U\$S 550.- per MTon.
Urea	U\$S 130.- per MTon.
Resorcinol Flakes	U\$S 2600.-per MTon.
Tannin extract	U\$S 500.- per MTon.

It is immediately seen that tannin in the international market fetches practically the same price as phenol, if allowance is made for recovery of the phenol drums although it is understood that normally freight for the bagged tannin extract would be somewhat cheaper than for the drummed phenol.

On the other hand technical grade urea is nearly four times cheaper than tannin so this fact would rule out the replacement of urea resins by tannin-formaldehyde binders, apart from the technical reasons as explained previously.

The replacement of phenol by natural tannin is therefore only marginally possible from a cost point of view, if both products were to be imported from abroad into a country that produced neither of them.

It would not be possible to economically import

tannin into a highly developed country producing phenol efficiently at international prices, but it would be of advantage to import it into a country producing phenol with a high protective tariff barrier for it having at the same time low tariffs for tannin extracts.

Another favourable situation for its use would be in a country producing natural tannins and having to import phenol or producing phenol at over international prices.

The above describes the economical possibilities when replacing part of the phenol by tannin in a co-condensed resin binder with formaldehyde. They do not offer a bright picture for the advancement of tannin extracts in the wood panel industry.

Regarding the use of quebracho tannin as an aggregate to phenol-formaldehyde glue mix, its use can be justified from a technical point of view, although not as a lesser cost item, as a shorter cure cycle can be obtained in plywood manufacture.

Being the leather tanning industry the major outlet for natural tannin extracts, its market price is governed to a great extent by the price structure in that industry prevalent in the chemical or wood panel fields.

Regarding the potential use of tannin extracts as raw material for wood panel resin binders, estimate may be drawn up from the 1970/1972 world panel production figures (100% solids).

<u>Plywood</u>	<u>MT/Year</u>
Urea-formaldehyde	515.000
Phenol-formaldehyde	620.000
<u>Particleboard</u>	
Urea-formaldehyde	1.635.000
Phenol-formaldehyde	130.000

Total Consumption

Urea formaldehyde	2.150.000
Phenol-formaldehyde	750.000

If tannin replaces from 20 to 50% of the phenol used in the corresponding binder, though co-condensation with formaldehyde, the potential for it would be between 90000 and 200000 thousand metric tons per annum.

If it is only as an aggregate (12% based on resin solids) in the plywood glue mix, the estimated potential is of 75000 metric tons.

The tannin extract industry can supply most of these needs with their present facilities.

7. CONCLUSIONS

The future of the natural tannin extracts as raw materials for wood panel resin binders will depend exclusively on the relative prices of phenol and tannin, as technical ways of using the latter have been found as shown previously, and the industry is capable of providing the product.

The highly industrial nations with efficient phenol production facilities will no doubt continue, for the time being, to use the phenol-formaldehyde resin binders due to their easier availability and relative lower cost. But rising petrochemical raw material prices will in a few years drastically change the present situation, barring any sudden petroleum crisis such as happened in 1973/74, when phenol prices jumped four-fold to finally stay at over double the prices previously prevalent. Therefore an extensive study into the use of tannin as phenol replacement should be made.

In the case of the lesser developed nations, which do not have an efficient petrochemical industry that can supply them with phenol, the need of natural resin binders, that can be obtained locally or at a lower cost through imports, is of utmost importance.

The replacement of part of their phenol needs by tannins obtained nationally will not only reduce the cost of the binders but will also help in their balance of payments through lesser imports.

In a similar way to some petroleum deficient countries, which have undertaken a programme to raise sugar cane for the ultimate production of ethyl alcohol as gasoline replacement, the countries without phenol should envisage a project for furthering the plantations of high tannin bearing plants, such as mimosa (black wattle), which will supply their internal needs as adhesive resin binders and, if a surplus were possible, permit its export to those industrialized nations unable to plant these trees, and which by that time will be in need of a replacement for part of their phenol requirements.

The tannin extract industry should endeavour to develop a grade of tannin, either of quebracho or mimosa origin, which could be used exclusively as raw material for the wood panel industry, and which should be set at a price level suited for this market. In this way a real incentive could be brought forth to justify the use of tannin extract as phenol replacement.

The binders should be manufactured by co-condensing phenol and tannin extract with formaldehyde, for exterior grade plywood and particleboard, to obtain maximum benefit from the use of these natural products; alternatively, the tannin extracts, preferably of quebracho origin, should be used as an aggregate to the plywood glue mix as an active extender and cure accelerator.

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