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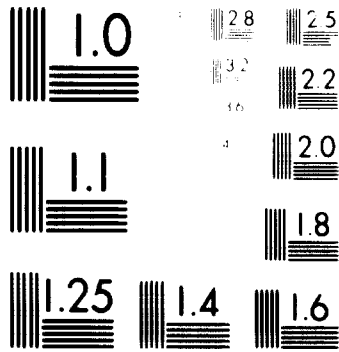
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United Nations Industrial Development Organization

Workshop on Adhesives used in the
Wood Processing Industries

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REVIEW OF

PAST RESEARCH ON UTILIZATION OF NATURALLY OCCURRING ORGANIC PRODUCTS AS

REPLACEMENT OF SYNTHETIC PHENOLICS IN WOOD ADHESIVES[1]/

by

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1. Introduction

Wood adhesives can conveniently be divided into two main groups, the natural, non-resin glues made by crude cooking processes from natural starches or caseins or from animal bones and hides, and the more recently developed synthetic, adhesive resins.

Adhesives now used by the wood working industries are predominantly synthetic resins almost entirely based on crude oil and natural gas and the main types of synthetic adhesives required by the wood-based panel industries are urea resins and phenolic resins, both thermosetting resins based on formaldehyde.

Phenolic resins are used in large quantities for plywood production, but they also play an important role in the manufacture of wood particle board, fibre board and laminated beams (phenol/resorcinol resins).

Phenolic resins have the property of producing bonding with excellent resistance to weathering. Exterior grade plywood (weather and boil proof) is for example dominated by the phenolic resins. These are alkaline-curing resins in the form of 40-50 per cent aqueous solutions, or as spray-dried powders which are dissolved before processing. Exterior wood particle boards are mainly bonded with similar phenolic adhesives. Synthetic urea-formaldehyde adhesives and natural glues produce bonding with only limited water and moisture resistance.

The present paper is concerned with past research on utilization of naturally occuring organic products as replacement of synthetic phenolics in wood adhesive resins, capable of producing anything similar to the weather resistant (water proof) bonding as produced by straight phenolic resins.

Phenol-formaldehyde resin adhesives and phenol/resorcinol-formaldehyde adhesives are based on phenol, resorcinol and formaldehyde. Formaldehyde is made by oxidation of methanol which in turn is obtained by oxidising natural gas. Phenol and resorcinol are primarily derived from benzene, a product of oil distillation. For each of these raw materials there are several conversion stages. The availability of synthetic, phenolic resins is dependent on the supply of the basic raw materials, crude oil and natural gas, and on adequate production facilities for all of the conversion stages. With world demand for wood panel products increasing, availability of synthetic, phenolic resins will depend upon the willingness of chemical manufacturers to install new plants. To do this, they must be satisfied with the return of their investment. At each stage of the conversion process from crude oil and natural gas to phenols and formaldehyde, several industries compete for products. The price at which synthetic phenolic resins can be produced is therefore set by the competing demand for the chemicals involved.

Because of low returns on investment in the chemical industry in the middle and late 1960's and early 1970's, companies were very hesitant to start new projects, and shortage of for example methanol, phenol and resorcinol occured. These shortages were heightened by the oil crisis in late 1973. Balance of supply and demand for

methanol may be reached in near future. Adequate capacity for
phenol and resorcinol production may be available in 1978, but
long-term supply is considered to be less stable than for metha-
nol, because benzene is increasingly in demand for use as addi-
tive for fuel (1).

The availability of phenols for wood adhesives over a long term
can, however, be better ensured by modifying the synthetic pro-
ducts with naturally occuring products. World wide shortage and
price increases of synthetic phenol and resorcinol have intensi-
fied the search for alternative lower cost materials based on
natural, non-petrochemical resources as replacement of phenolics
in adhesives for the wood working industries.

Research in connection with the development of phenolic adhesives
from natural occuring sources has from time to time been reported
from various parts of the world. The phenolic components in commer-
cial, vegetable tannin extracts, other wood and bark extracts and
lignin-related products such as the waste product from paper mills,
spent sulphite liquor (SSL), have been suggested as natural phe-
nolic sources for partial or full replacement of phenol in phenol-
formaldehyde adhesive resins for the manufacture of plywood and
wood particle board. The use of these natural products as replace-
ment of resorcinol in resorcinol-based formaldehyde adhesives as
well as accelerators for the cure of phenolic adhesives has also
been considered.

The development of phenolic adhesives from spent sulphite liquor
and bark extracts has long been a goal for chemists. The incentive
for this has not only been the possibility to find low-cost sources
for phenolics, but also the need to reduce pollution by SSL dis-
charged into water courses and to find use for the large quanti-
ties of bark being disposed.

Commercial, vegetable tannin extracts, which are mainly manufac-
tured for the purpose of converting animal skin into leather, are
available in the form of spray-dried powder. The substitution of
natural phenols derived from various tannin extracts and lignin-
derived products for synthetic phenols is reported to be an
established commercial practice in a number of countries, and
significant economics are reported to have been obtained by their
use. Of particular interest are resources available within the
adhesive consuming country, thus benefiting both the domestic
product and balance of payments of the country.

If any of these natural sources are to be relied on as replace-
ment for phenols in wood adhesives, the source of supply must be
identified and the scale and timing of investment geared to the
industrial requirement. The adhesive requirement of the wood
working industry should therefore be assessed and kept under re-
view.

Synthetic adhesive resins like phenol resins are, in the devel-
oped countries, usually manufactured in large, integrated chemi-
cal complexes whereas the developing countries generally have to
rely on imported raw materials such as methanol or formaldehyde
and synthetic phenols. As a result of relatively small plant

capacities, the cost of synthetic resins in developing countries are comparatively higher and their wood-based products therefore less competitive.

There are useful natural sources of phenols available in many developing countries. Particular attention should be given to research and dissemination of information on the development of adhesives less costly in terms of the resources available in these countries. A wider exchange of experience and information on technologies and uses of such adhesives was called for at the FAO-organized congress "World consultation on wood-based panels" in New Delhi in February 1975 (53).

2. Commercial, vegetable tannin extracts as partial or full replacement of synthetic phenol in wood adhesives

Tannins are derived mainly from trees, especially from barks and woods, but occur widely in plants generally. Even though many plants produce tannins, properties and yield vary, and only a few tannin extracts are available commercially. Their primary use is for converting animal skins into leather.

The chemistry of the vegetable tannins has been surveyed in detail by White (2) and by Endres (3), both of whom have provided exhaustive bibliographies. Vegetable tannin extracts are described as of two kinds, hydrolyzable tannins and condensed tannins.

Hydrolyzable tannin extracts are mixtures of sugars with phenolic carboxylic acids (gallic acid or ellagic acid) and substances built up from these acids through ester linkages to sugar residues. The sugar is usually glucose, but polysaccharides or branched sugars are also known to occur. The ester linkages in these tannins are readily hydrolyzed by the action of acids and alkalies or simply by warm water.

Condensed tannins contain complex mixtures of "polyphenols" (i.e. polynuclear, polyhydric phenols) which are capable of forming insoluble phlobaphenes. The detailed chemistry of the condensed tannins is only incompletely known, owing to their extreme complexity and the difficulty of separating their components. However, the general nature of the substances present is clear, and it can be stated with certainty that the basic structural unit consists of resorcinol and phloroglucinol-groups connected by short, aliphatic chains to a similar number of catechol and pyrogallol nuclei (4).

It should be kept in mind that the precise composition of a vegetable tannin extract varies with, and is characteristic of, the particular plant from which it is extracted, and that the complexity of composition influences the properties of the extracts. Thus, it would be without meaning just to refer to "tannin" or "tannin extract" without giving the source from which the tannin is extracted.

The most important commercial sources of condensed tannins are extracts from: The heart-wood and the barks of mimosa (wattle), Acacia Mollissima, and the heart-wood extract of quebracho, Scinopsis Lorentzei.

The bark extract of mangrove, Rhisophora and Bruguiera spp., is also commercially available, but has limited importance as tanning material.

The larger commercial source for hydrolyzable tannins is the extracts from the heart-wood and sap-wood of the chestnut tree, Castanea spp.

Other sources of commercial, vegetable tannin extracts, both condensed and hydrolyzable, are described by White (2).

Tannin extracts of quebracho are produced in Argentina and Paraguay, Argentina being the main producer, and of mimosa in South and East Africa as well as Brazil, South Africa being the main producer.

The major proportion of the chestnut wood tannin extracts comes from France and Italy.

The extracts are now available as spray-dried, water soluble powders.

Condensed tannin extracts have long attracted interest as a potential natural source of phenolic substances which may be reacted with formaldehyde to form water proof wood adhesives. Hydrolyzable tannins have, until recently (5), been considered to be of little interest as replacement of synthetic phenols in water proof, phenolic adhesive resins.

The patent literature shows the attention that has been given to the condensed tannin extracts as component in phenol-formaldehyde resins. The first patent (6) was applied for as long ago as 1914, in some later ones there would appear to be a good deal of overlapping. McCoy (7) in 1918, used a tannin as both a condensing agent and a reactant in the phenol-formaldehyde reaction.

In 1932, Kessler (8) suggested tannins as alternatives to dihydroxybenzenes to accelerate the curing of phenolic moulding resins. Morgan and Magson (9) prepared in 1937 laminated boards from paper successively impregnated with hexamine and one of the three tannins catechin, quebracho and gambier. In 1940, Brown and Angel (10) suggested a tannin and an aldehyde or an initial condensation product of these substances as hot-press wood adhesive. Phillips and Rottsieper (11) made plastic materials in 1942 by adding paraformaldehyde, or hexamine, to ground mimosa, or mangrove barks, or quebracho wood. Mimosa, valona and quebracho tannins have been used, by Bartlett in 1945, as substitute for phenol in moulding powders and laminates (12).

Valuable information on wood and bark extractives in general and on tannin based formaldehyde adhesives for wood has been reported from Australia (13-38), largely through the work of the Commonwealth Scientific and Industrial Research Organization (C.S.I.R.O.), covering extracts of quebracho, mimosa, mangroves, Pinus Radiata (pine) and certain species of Eucaluptus, the pioneering work being done by Dalton (13) in the late 1940's.

The first aim of the work was the development of highly reactive low-cost exterior type adhesives for plywood, although the possibility of using tannin-formaldehyde resins for bonding other wood products was recognized at an early stage (28).

In 1950 Dalton (13) reported extensive work on the reactivity of condensed tannin extracts from six species including commercial wattle extract. All the tannins reacted with formaldehyde to form resins and the rates of condensation were assessed by measuring gelation times. The tannins from four species formed strong water resistant bonds with wood when used as hot-press adhesives. Two of these species also gave bonds when used as cold-press adhesives,

but of lower strength; water resistance was superior to that of
a urea-formaldehyde adhesive. However, the use of alcoholic so-
lutions of the extracts in order to control viscosity raised
problems with respect to possible commercial use.

Dalton carried out further work on viscosity control with tannin
extracts (wattle and others), and in 1953 (14) reported that
tannin solutions after heating with sulphites have lower visco-
sities and are suitable for the preparation of adhesives for use
with mechanical roller spreaders. The sulphited tannin solutions
were tested as adhesives for plywood and all gave bonds which
were resistant to 6 hr immersion in boiling water, although wood
failures were low.

In England, research by Knowles and White, published in 1954 (4),
was concerned with commercial quebracho and mimosa extracts. Their
work covered the synthesis of adhesives made wholly from que-
bracho or mimosa extracts and formaldehyde, as well as the partial
replacement of synthetic phenol-formaldehyde resins for water
proof adhesives.

Plomley (15) reported in 1957 that simple hot-press adhesive for-
mulations based on aqueous solutions of commercial mangrove tannin
gave strong bonds resistant to immersion in boiling water for 6 hr
with some veneer species, but wood failures were not considered
sufficiently high. Tests with commercial wattle tannin gave more
consistant results and higher wood failures. The adhesive proper-
ties of wandoo[1] extract were less satisfactory.

It was shown that adhesive properties could be improved by forti-
fication with 10-30 per cent synthetic phenol-formaldehyde and
resorcinol-formaldehyde resin on the weight of the tannin-form-
aldehyde resin. High values for shear strength were then obtained
when tested dry and wet after immersion in boiling water for 6
or 72 hours. The amount of fortifying required to give a satisfac-
tory bond is dependent on the type and quality of tannin, kind
of resin and wood being bonded (28).

In 1958 in Africa, Parrish (29) reported that good particle boards
may be made with mimosa tannin-formaldehyde resins.

The effect of soluble salts in decreasing the gelation time of
wattle and mangrove tannin solutions with formaldehyde was re-
ported by Plomley in 1959 (20). Five per cent manganese acetate
added to a wattle tannin extractive improved bond quality.

Hillis and Urbach reported the same year (30) on the reaction of
catechin with formaldehyde under different conditions. The use
of catechin as a model compound for condensed tannins was dis-
cussed. They also studied the reaction of wattle and mangrove
polyphenols with formaldehyde at various pH and under different
conditions of temperature and time (31).

In 1963 (22) a paper was presented to UNCSAT summarizing
C.S.I.R.O.'s work on properties of wattle, mangrove, wandoo and
pine tannins, the application of tannin-formaldehyde adhesives
to plywood manufacture and the results of exploratory tests of
wattle tannin adhesives for bonding particle board.

1) Eucalyptus wandoo

In 1963 a representative of an Australian plywood manufacturer reported to the International Consultation on Plywood and other Wood-Based Panel Products, held by FAO in Rome, that wattle tannin adhesives had been adopted for exterior plywood manufactured by his firm (28).

In 1966 (23) a report was made on studies of physical and chemical properties of wattle tannin adhesive formulation and properties, details of the development of the phenolic fortifying resins reported in 1957 (15), and plywood and particle board tests conducted under laboratory and factory conditions.

The high viscosity of aqueous solutions of condensed tannins has been a problem. It was found that the viscosity of solutions of quebracho extract can be reduced by the addition of small proportions of synthetic phenol, urea and some other organic compounds. A similar effect has been observed with aqueous solutions of other tannins such as wattle and pine (28).

Wattle tannin adhesives for plywood manufacture differ from synthetic resin adhesives as they, especially when the veneer moisture content is low, tend to dry out faster and thus giving insufficient flow in the hot press (28). On the contrary, at high veneer moisture contents, the adhesive tend to penetrate veneers.

In 1969 the properties of particle boards made under laboratory conditions, from pine wood particles and two of the commercially produced, condensed tannins, wattle and quebracho, were reported (24). As with the plywood formulation the tendency is to decrease the proportion of fortifying resin. Under laboratory conditions unfortified wattle tannin adhesives have given satisfactory bonds with pine, which is the main specimen used for particle board manufacture. Generally, the properties of tannin-formaldehyde bonded boards were equivalent to those of synthetic alkaline phenol-formaldehyde boards at the same active adhesive content. Higher mat moisture contents are necessary when using the tannin adhesives than in the case with synthetic resin adhesives; moisture contents of about 25 per cent for surface layers and 17 per cent for core have been used (28). It is not clear how such high moisture levels are handled in the hot press. Nevertheless, wattle tannin extracts is reported to have been used industrially for some years by the particle board and plywood industries in Australia, South Africa and India.

Quebracho tannin extract is used commercially in many countries including Argentina, Brazil, Finland, U.K. and U.S.S.R. Thus, both acceleration of cure and improvement of bonding strength are reported in Finland where quebracho makes up 10-20 per cent of the total glue solids in highly extended phenolic glue mixture used for plywood (39). However, as quebracho has high reactivity with formaldehyde, it is not used alone because of problems with pot life and viscosity (40, 41).

It would appear that development has hardly reached the stage where a completely satisfactory and easy-to-use commercial adhesive resin product, utilizing commercial, condensed tannin extracts as the only phenolic compound, could be marketed. Two main

reasons for this has been indicated in certain unpublished work
(32). Firstly, the pot life is short; associated with this, the
ratio of pot life to curing time (at temperatures used in board
manufacture) is relatively low. The explanation is probably that
the tannin-formaldehyde resins contain molecules of a wide range
of size and structure, a small per centage of highly reactive
molecules (as in the fortifying phenolic resins) being sufficient
to cause fast rise of viscosity and termination of pot life at
room temperature, whereas satisfactory curing requires also the
crosslinking of larger and less reactive molecules. Thus, it was
believed (33) that the crosslinking of condensed tannin molecules,
despite their greater reactivity with formaldehyde than synthe-
tic phenol, suffered from steric hindrance due to molecular size
and shape. Therefore, the curing of condensed tannin adhesives
would benefit by addition of smaller reactive units which could
form links between the large tannin molecules. Methylolphenol
compounds could serve this purpose, and low molecular-weight
phenol-formaldehyde resins have therefore been used successfully
as the linking agent for adhesives based on condensed tannins.

Secondly, the condensed tannin resins have been reported to lack
good spreading and wetting properties (28). However, in spite of
these shortcomings high joint strengths have been obtained with
resistance to water, including boiling water, as for synthetic
phenol-formaldehyde adhesives.

As mentioned previously, hydrolyzable tannins have, until recent-
ly, been given little attention as natural source for the replace-
ment of synthetic phenol in wood adhesives. In 1975 Kulvik re-
ported results obtained in Malaysia with chestnut wood tannin
extract as chemical replacement of phenol in normal, alkaline
phenol-formaldehyde adhesives for plywood (34). Results obtained
by the plywood factories show that up to 50 per cent of the syn-
thetic phenol could successfully be replaced by chestnut wood
tannin extract (as dry powder), meeting the requirements accord-
ing to BS 1455 for WBP gluing. The chestnut wood tannin modified
phenolic resin has the same solids content, pH and viscosity as
the unmodified resin and the same filler, degree of extension
and glue spread was used. Properties like pot life, shelf life
(storage life) were the same as for the pure, synthetic resin and
results obtained indicated that the hot pressing time could be
reduced. The chestnut tannin modified adhesive resin was used under
the same conditions of plywood manufacture as the unmodified resin;
there were no problems with glue spreading, wetting properties or
veneer moisture content. However, increasing degree of phenol re-
placement showed higher sensitivity towards variations of condi-
tions during plywood manufacture. The results obtained by the ply-
wood factories showed that the average wood failure (after testing
according to BS 1455, that is boiling samples in water for 72 hr)
decreased from 75 per cent (60-90 per cent) to 55 per cent (30-80
per cent) when the synthetic phenol replacement was increased from
0 per cent to 50 per cent.

In hydrolyzable tannin extracts, such as chestnut wood tannin
extracts, gallic acid and ellagic acid are potential resin forming
agents with formaldehyde. These acids easily decarboxylate under
the action of heat to reactive polyhydric phenols. For example
gallic acid produce pyrogallol which is reactive with alkaline

formaldehyde. Sugar from the tannin compounds, (esters of phe-
nolic acids with sugar) and from the non-tannin compounds
(mixture of phenolic acids and sugar) will also take part in
the chemical reactions during the adhesive resin formation. The
idea of using sugar as modifier for alkaline phenol-formaldehyde
wood adhesives is not new, U.S. Patent No. 1 959 433 was issued
to Loetscher in 1934 (35). However, Loetscher's process was
never realized commercially because of its uneconomical prepa-
ration (36). In 1955 a screening program for the utilization of
sucrose in phenolic resins was begun by Bjorksten Research
Laboratories. They succeeded in producing a sucrose-modified
phenolic resin which appeared to have attractive adhesive pro-
perties (37). The study was transferred to Herstein Laborato-
ries in 1959, and in 1962 Chang and Kononenko report (36) that
50 per cent of the synthetic phenol used in a regular, alkaline
phenol-formaldehyde resin for plywood has been replaced success-
fully by sucrose and test results for wet strength are reported
to be comparable to, or better than, straight phenolics. The
sugar was found to be completely chemically bound and to form
part of the phenol-formaldehyde resin molecules.

Attention should here be given to a report (38) regarding the
utilization of for example tannin extracted chestnut wood for
the manufacture of particle board, and to a study on the influ-
ence of commercial tannins and crude wood extracts on wood-glue
bonds by Plomley, Hillis and Hirst (27).

3. Other vegetable tannin extracts, especially from woods and barks, as partial or full replacement of synthetic phenol in wood adhesives

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A large number of the compounds in extractives from different plants has been identified and they represent many classes of organic compounds. Extractives are the non-structural or second-ary constituents of plants and they can usually be removed with neutral solvents although dilute alkali is sometimes necessary. The polyphenolic compounds, which do not include lignin, are the most common components (25). Barks are generally much richer than wood in quantity and complexity of extractive components. Chemical processing of bark is limited and large quantities of it are unused and must be disposed of. Moreover, such disposal is becoming more of a problem due to increased restrictions on incineration of bark residues (51).

Use of phenolic components of bark- and wood extracts in pre-paring adhesive compounds used in plywood and particle board manufacture has been proposed from time to time. Dalton, Australia, in 1950 (13), was the first to report work on the use of wood- and bark extracts to produce formaldehyde resins as ply-wood adhesives. His work covered adhesive properties of extracts from six species including commercial wattle extract and extracts from bark and wood of species of Callitris and Eucalyptus. How-ever, the use of alcoholic solutions of the extracts in order to control viscosity raised problems with respect to possible com-mercial use. Dalton carried out further work on viscosity control with tannin extracts, and in 1953 (14) reported that tannin solu-tions of wattle, Eucalyptus and Pinus Radiata, after heating with sulphites, have suitable viscosities for the preparation of ply-wood adhesives for use with mechanical roller spreaders. He ob-tained bonds which were resistant to 6 hr immersion in boiling water, but wood failures were low. Plomley (15) reported in 1957 that simple hot-press adhesive formulations based on mangrove (Rhizophora and Bruguriera spp.) extracts,, wattle and wandoo (Eucalyptus wandoo and E. Accedens) gave strong bonds resistant to boiling water for 6 hr with some veneer species. The wood fail-ures were not considered sufficient high, with commercial wattle tannin giving more resistant results. In 1960 Herzberg (17), in a report dealing with plywood adhesive from Pinus Radiata bark extract, claimed that an adhesive can be prepared at room tempera-ture that meets standard specifications for weather proof and boil proof adhesives.

From Indonesia, Brandts in 1952 (44) reports that a strong, water resistant plywood adhesive could be produced from mangrove bark tannin formaldehyde resin.

In India, research by Narayanamurti and co-workers (83-89) starting in the early 1950's has included tannin extracts from tamarind seed, tea waste, species of trees growing in Asiatic mangrove forests and miscellaneous timbers as adhesives for plywood. None of these adhesives, however, seem to be suitable for commercial application without further development. Accord-ing to a recent report (52), tannin-formaldehyde adhesives from

wattle bark extract, mimosa wattle and other extracts in combination with proteinous materials have given better results. The proteinous material is said to increase the pot life and to reduce penetration into veneers.

In Canada, MacLean and Gardner in 1952 (43) proposed using tannin extracts from western hemlock bark with formaldehyde as plywood adhesive. Herrick and Bock (U.S.A.), in 1958 (42), suggested a phenol-formaldehyde resin instead of formaldehyde.

In New Zealand in 1960, Hall, Leonard and Nicholls (45) reported on experiments producing wood particle board using Pinus Radiata bark extract and formaldehyde.

Then in U.S.A., Anderson, Breuer and Nicholls in 1961 (46) used ponderosa pine, tanoak and douglas fir extracts in combination with formaldehyde as adhesive for particle board. The physical properties of the boards were reported to be similar to those of boards made with urea-formaldehyde resins.

So far, available information on proposed tannins and tannin-like materials extracted from woods and barks indicates that none of them are equivalent to commercial tannin extracts and that there is no general incentive to use any of them commercially as replacement for synthetic phenol (50). Although many investigators have endeavoured to obtain for example boil proof plywood with bark extracts, these attempts have been largely unsuccessful either from a plywood performance viewpoint or due to excessive cure time requirements or other economic reasons. In general, where success has been reported, the level of utilization of the extract material has been quite low.

In recent investigations (47, 48, 49 and 50), reported in 1974 and 1975 by Anderson, Wong and Wu in U.S.A., bark extracts of white fir, douglas fir, western hemlock and ponderosa pine were evaluated as bonding agents for wood particle board. Wood particles were sprayed with concentrated bark extracts, followed by the addition of paraformaldehyde, and processed into board. Formaldehyde, released during the hot-press cycle, is reported to react in situ with polyphenolic compounds present in the extract and to form water proof bonding comparable to some synthetic phenolic resin bonded exterior-type particle board at reduced cost of production. It was in this connection suggested that developing countries should be encouraged to analyze their softwood- and hardwood barks as possible sources of low-cost phenolics to be used in the manufacture of water proof particle board (51).

Attention should also be given to the possibility of making bark boards, without using synthetic adhesive resins (81). This can be done by utilizing the principle of bark extractive-lignin polymerization at high temperatures, 250-300°C (480-570°F). Grooved platens on the hot press are necessary for releasing the steam. The bark boards were then found to have the properties of exterior grade particle board. At these high press temperatures the bark undergo simultaneous chemical degradation and polymerization reactions. This technique at the present time

(1975) is only of an exploratory nature and is subject to the restriction of its high temperature requirement. However, modern technological progress, such as the adaption of radiofrequency or microwave heating systems, could offer an opportunity for the early utilization in industrial production.

4. Research on utilization of lignin and lignin-related products in wood adhesives

Lignin, constituting about 25 to 30 per cent by weight of the dry weight of wood, is a high molecular weight polymer having structural properties similar to phenolic resins. There are two possibilities of introducing lignin into the chemistry of resins;
a) lignin is used in its high molecular weight state without any degradation
b) lignin is degraded to low molecular weight phenolic compounds and these are converted into resins in a well defined manner.
The first possibility is cheap but unclear, the second is more expensive but clear.

Since lignin is the natural binder in wood, it is logical to utilize it as a binder for reconstituted wood. The development of a wood adhesive from lignin, especially in the form of the waste product from paper mills, spent sulphite liquor (SSL), has long been a goal for chemists. The incentive for this has not only been the abundant availability of SSL as a low-cost waste product, but also the need to reduce the pollution when SSL is discharged into water courses. The recent world wide shortage and price increases for synthetic phenolic adhesives have made this goal more attractive (54).

There is at present a number of patents (55-64) in Canada, the U.S. and European countries, describing methods of preparing a resin binder from SSL for composite wood products. Unfortunately, either extensive chemical modifications have resulted in the SSL binder being so costly as the conventional synthetic resins, or the SSL binders have demanded a far more complex manufacturing process. These reasons have rendered the utilization of SSL economically and technologically impossible (54).

In the mid-1960's, Pedersen of Denmark (58) developed a process for making water proof particle board with SSL binder. This development required a long pressing time and an even longer subsequent autoclaving to convert the SSL binder to a water proof bond. Thus, the economical advantage of using the inexpensive SSL binder was largely offset by the cost of long press time and autoclaving at high pressure. Furthermore, it has been reported that a Finnish plant built in 1970 to use the Pedersen process discontinued production of SSL particle board because of technical problems developed during high pressure autoclaving (54).

In 1971 in Germany, Roffael and Rauch (65) investigate the influence of pressing time and pressing temperature as well as the hot stacking on the physical and mechanical properties of particle boards developed with SSL as binder. The results show that the pressing time has no significant influence on the physical and mechanical properties as long as temperatures below $180^{\circ}C$ are used. Even though for example very low thickness swelling was found, this could only be achieved through a hot stacking treatment at $200^{\circ}C$ for several hours. Another study reported in 1971 (66) relates to a new and relatively fast method for the production of particle board using SSL as binder. The method is

based on the addition of an acid-tolerant phenol-formaldehyde resin of the type "Novolac" to increase the binding properties of SSL to obtain a practically water insoluble thermosetting adhesive, without using post-thermal treatment. They report that this method made it possible to produce particle board with higher mechanical properties than those developed after the "Pedersen technique". A combination of contact- and radiofrequency heating was used. In 1973 Roffael and Rauch report on evidence that sodium lignin sulphonates (prepared by cation exchange of calcium and magnesium lignin sulphonates) can be used as partial substitute or extender for conventional alkaline phenolic resins for particle board and that 50 per cent replacement produce particle boards still having mechanical properties well above the German standards (67).

More recently, in 1974 Roffael et al. (68) report that sodium lignin sulphonates can be used as an extender or substitute for alkaline phenolic resins to produce plywood if certain conditions, such as pressing temperature and pH-value, are adhered to. At a pressing temperature of 140°C, about 20 per cent of the synthetic phenolic adhesive can be substituted, producing plywood fully equivalent to those produced from phenolic resin alone. At a pressing temperature of 190°C, about 30 per cent of the phenolic resin could be substituted without impairing the properties of the boards significantly. In another report (69), they deal with a combination of SSL and phenolic resin in acid medium, as plywood adhesive, and found that the rate of condensation of especially prepared lignin sulphonates by thermal treatments in an acidic medium and in the presence of phenolic resins can be greatly increased. At a pressing temperature of 190°C, about 30 per cent of the phenolic resin could be substituted without reducing the properties of the boards markedly. However, at a pressing temperature of 165°C, the substitution of more than 10 per cent of phenolic resins leads to a considerable decrease in the physical- and technological properties.

The manufacture of exterior particle board has been inhibited by the relatively high cost of phenolic resins and also by the longer press time than required by urea-formaldehyde resins. Phenolic wafer boards have been reported (70) to become increasingly accepted since their first commercial production in Canada in 1961, the success was due to its low (3 per cent) content of phenolic resin, possible because of the large particles used. Shen, in Canada in 1974, reports (70) that SSL, modified with a strong mineral acid (sulphuric acid), can be used as a resin binder for exterior grade wafer board with about the same hot press time and physical and mechanical properties as those found in commercial, phenolic-bonded wafer board. He reported on a potential saving of around 25 per cent on material cost, using 4 to 5 per cent SSL (powder) and maximum 1 per cent sulphuric acid.

Shen, in 1975 extended his work to include acidified SSL binder for wood particle board (54) and reports that promising results are obtained. He also suggests the possibility of making panel products from bark, bagasse and rice hull, using SSL binder.

However, the relatively high acidity produces undesirable effects.
Acid reduces wood strength as a result of wood hydrolysis. The
hydrolysis of wood in the presence of strong acid, particularly
under hot pressing, will proceed at a rapid rate. High acidity
in particle board may also have a long-term destructive effect
on the wood. In addition, there may be a corrosive effect on
nails and other hardware used to fabricate articles from the
panel. A post-treatment may therefore be necessary to reduce
the acidity.

Moreover, SSL as potential low-cost phenolic source is now run-
ning short as most countries convert their plants to the sul-
phate process (77). Most of the SSL available is now being used
as cattle feed supplement and higher value industrial products
(50).

In India in 1962, a study was made by Narayanamurti, George and
Joshi (71) on phenolic wood adhesives with lignin liberated by
enzyme treatment of sawdust through fungal attack. It is con-
sidered that lignin in the decayed wood is largely in the freed
condition which flows and acts as binder. The work continued
(72) and sawdust of different species of wood which had been
subjected to prolonged action of fungi was employed, the fungi
destroying the cellulose leaving a lignin rich residue. 30 to
60 per cent of the phenol in plywood adhesive is reported to be
replaced successfully with the treated sawdust. Recent experi-
ments with SSL as replacement of synthetic phenol in plywood
adhesives (72) have indicated that 60-80 per cent of the phenol
could be replaced with satisfactory results.

Throughton et al. (73, 74) have adopted an entirely different
technique in utilization of lignin in resin formation. They
carried out hydrogenolysis of lignin followed by demethylation
and found that 4-methyl-catechol, one of the resulting products,
is an excellent compound for the preparation of formaldehyde
resins. Quality of bonds made with this resin is reported to be
comparable to those of synthetic phenolic resins.

Demethylation of lignin is expected to result in increasing
phenolic groups and therefore higher reactivity with formalde-
hyde. On this basis, studies on demethylation of lignin and its
effect on resin forming properties are reported to have started
in India (72).

The alkali-catalyzed reactions of formaldehyde with lignins have
been described by Marton et al. (75). General nature, structure,
chemistry and occurance of hardwood lignins is briefly reviewed
by Bleam and Harkin in 1975 (76) with references to latest de-
tails in recent publication.

5. Vegetable tannin extracts as replacement of synthetic
   resorcinol in resorcinol based adhesives and as accelera-
   tor for the cure of phenolic adhesives

Resorcinol, much more reactive than phenol, has the property of
producing cold-setting adhesives with formaldehyde. Resorcinol
is therefore also used as accelerator for curing of hot-setting,
phenolic adhesives.

As early as in 1932 Kessler (8) suggested condensed tannins as
alternatives to resorcinol to accelerate the curing of phenolic
moulding resins.

In 1950 Dalton (13) reports on cold-setting wood adhesives pre-
pared from tannin extracts of wattle and of Callitris, and form-
aldehyde, to produce water resistance superior to the cold-set
urea-formaldehyde adhesives.

In 1960 in the U.S., Herrick and Conca (78) report that a highly
reactive extract obtained from western hemlock bark can be used
in the formulation of cold-setting water proof wood adhesives,
so as to permit a reduction in adhesive costs and to contribute
to the upgrading of our basic forest resource - wood. 30 to 60
per cent (dry) extract is mixed with a resorcinol formaldehyde
resin and additional formaldehyde to produce an adhesive which
meets pot life and assembly-time requirements of wood laminated
(glulam beams) industries. Tested bonds passed requirements of
the major performance standards.

More recently, in 1973, Plomley et al. (79) report successful
laboratory tests of wattle and Pinus Radiata tannin adhesives
for laminating timber when using radiofrequency heating to cure
the adhesives.

On account of the acute shortage of resorcinol in South Africa
by the end of 1973, a substitute for resorcinol-based adhesives
used in manufacturing glulam beams was urgently required.
Sharfetter (33) reports that a commercial phenolic plywood ad-
hesive, or wattle tannin-formaldehyde adhesives modified with
small quantities of phenol and resorcinol, were found to be
suitable to this purpose provided the beams were heated during
the curing stage. The wattle tannin adhesives were preferred
because the temperatures required for cure were lower. It was
essential to maintain a sufficiently high relative humidity in
curing chambers to prevent the timber from becoming dried out.
Facilities for curing at elevated temperature in laminating
plants is considered to be economically justified, because the
adhesives tested cost much less than conventional laminating
adhesives based on resorcinol.

Quebracho is reported to be in commercial use in combination
with paraformaldehyde with good results in Finland as accelera-
tor for the cure of highly extended phenolic plywood resin (41).
Quebracho makes up 10 to 20 per cent of the glue solids.

Chestnut wood tannin extract is, since 1975, in commercial use in Malaysia as accelerator for the cure of ordinary, alkaline phenol-formaldehyde adhesive for plywood (80). Without influencing properties like pot life, assembly time or storage life, the curing time was reduced to such an extent that the hot pressing capacity, as an average for 18 plywood factories, could be increased by 60 per cent. The veneer moisture content before glue application was in the range of 4 to 14 per cent.

The following glue formulation was used:

Phenol-formaldehyde resin 1)	:	100 p.b.w.
Filler (extender)	:	30 "
Chestnut wood tannin extract (powder)	:	6 "
Water	:	5 "
Total	:	141 p.b.w.

1) Total solids content: 42 per cent, pH: 12.8 - 13.2.
  (p.b.w. stands for parts by weight)

Thus, commercial, condensed tannin extracts as well as bark extracts seems to be suitable as partial or full replacement of resorcinol in cold-setting adhesives whereas chestnut wood tannin extract (hydrolyzable), in addition to such extracts, produces good results as accelerator for the cure of phenol-formaldehyde adhesives. Tannin- and bark extracts can therefore be used with profitable results not only when the phenol prices are high.

6. Brief introduction to the chemistry of lignin and wood extractives and their adhesive resin forming properties

There are about 2000 wood species known at present. All woods contain cellulose, hemicelluloses and lignin but structure and composition vary. In addition, there are a vast number of extraneous, organic compounds (also termed extractives), present in some woods and absent from others. Both the wood and bark are products of a living organism, the tree. As such, their structure and composition will also vary, depending on just what has happened to the tree during its lifetime; the conditions of growth.

Cellulose and hemicelluloses are carbohydrates (polysaccharides), which are hydrolyzed by strong mineral acids to water-soluble sugars; lignin is resistant to these acids. Although the differentiation between lignin and the carbohydrates is simple, that between lignin and constituents in the extractives, such as condensed tannins, is more difficult.

The structure of lignin is still only incompletely known and the term "lignin" cannot be considered to be the designation of a constitutionally defined compound; it is rather a collective term for a group or system of high-molecular, amorphous compounds that are chemically very closely related in the same sense as are other natural high-molecular products such as cellulose, hemicelluloses, starch and proteins. Lignin may perhaps be defined as that incrusting material of the plant which is built up largely of methoxylated p-hydroxyphenyl-propane-stones with varying degrees of oxidaticn of their side chains (fig. 1.); but how these building stones are fused together is still unclear.

```
        OH
        |
  H -  C  - H          a)  R = R' = H
        |
  H -  C              b)  R = OCH_3, R' = H
        ||
        C  - H         c)  R = R' = OCH_3
        |
        4
      5     3
      6     2
    R'      R
        1
        OH
```
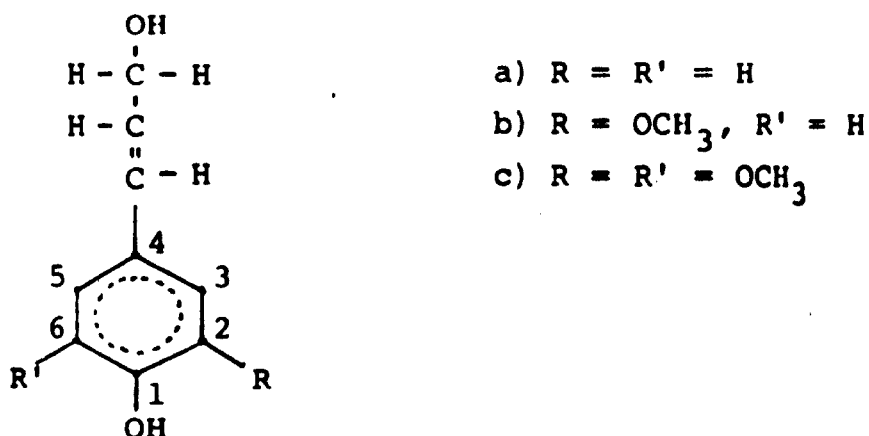
Fig. 1.

Only the 2- and/or 6-position of the phenolic nuclei are theoretically reactive with alkaline formaldehyde. Experimental results show that about half of the phenolic nuclei in lignin are unsubstituted and reactive (75), and largely only in one position of the nuclei, the 2- or 6-position.

To increase the reactivity of lignin with formaldehyde,
Throughton et al. (73, 74) carried out hydrogenolysis of lignin
followed by demethylation and found that 4-methyl-catechol
(fig. 2.), one of the resulting products, is an excellent mate-
rial for the preparation of formaldehyde resins as they have
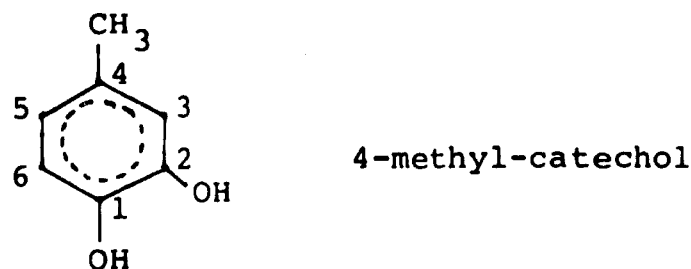three possible reactive sites in the nuclei:

4-methyl-catechol

Fig. 2.

The 3- and 6-positions are more reactive than the 5-position.
Some native lignins also contain a few catechol units.

The reaction of SSL (lignosulphonic acid) with formaldehyde have
been studied by Borisek and Polcin (82) and others, and a maxi-
mum of 8-9 per cent formaldehyde combined with lignin under op-
timal conditions.

Condensed tannins differ from lignin for example through their
lack of or negligible content of methoxyl groups but possess poly-
phenolic structures similar to that of lignin. Water-soluble con-
densed tannins occur especially in the bark and heartwood of trees.
The detailed chemistry is not completely known, owing to their
extreme complexity and the difficulty of separating their compo-
nents. However, the general nature of the substances present is
clear and the basic structural unit consists of resorcinol- and
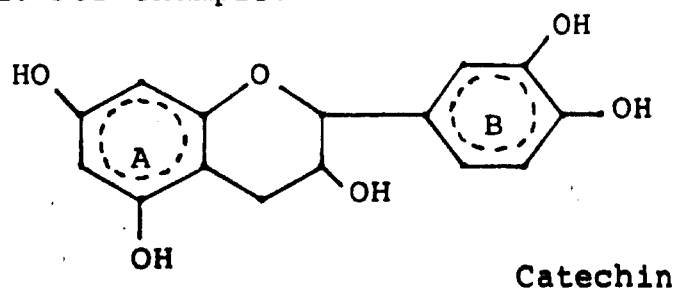phloroglucinol-groups connected to catechol- and pyrogallol-
nuclei. For example:

Catechin

Fig. 3.

As indicated by the structure, the A-ring is a resorcinol group
(2 reactive positions with formaldehyde) and the B-ring a cate-
chol nuclei (2 reactive positions with formaldehyde). However, it
cannot be concluded that the A-ring and the B-ring react with form-
aldehyde as free resorcinol and free catechol (30).

Hydrolyzable tannins are built up from polyphenolic acids (gallic acid, ellagic acid) and sugar (glucose) through ester linkages. For example:
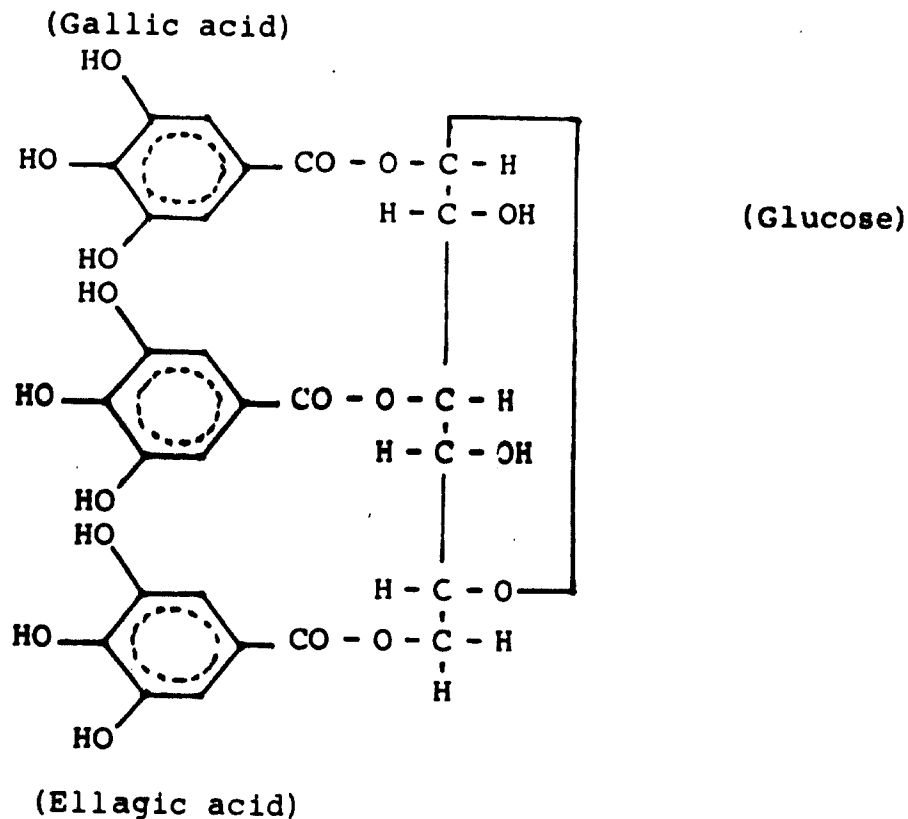
(Gallic acid)

(Glucose)

(Ellagic acid)

Fig. 4.

Hydrolyzable tannins are easily hydrolyzed by dilute alkali, acid or warm water. Both gallic acid and ellagic acid decarboxylate by the action of heat. Thus, gallic acid is easily converted to pyrogallol with positions in the ring capable of adding alkaline formaldehyde. Also sugars, such as glucose, react with formaldehyde and methylolphenols (36) to participate in the resin forming reactions.

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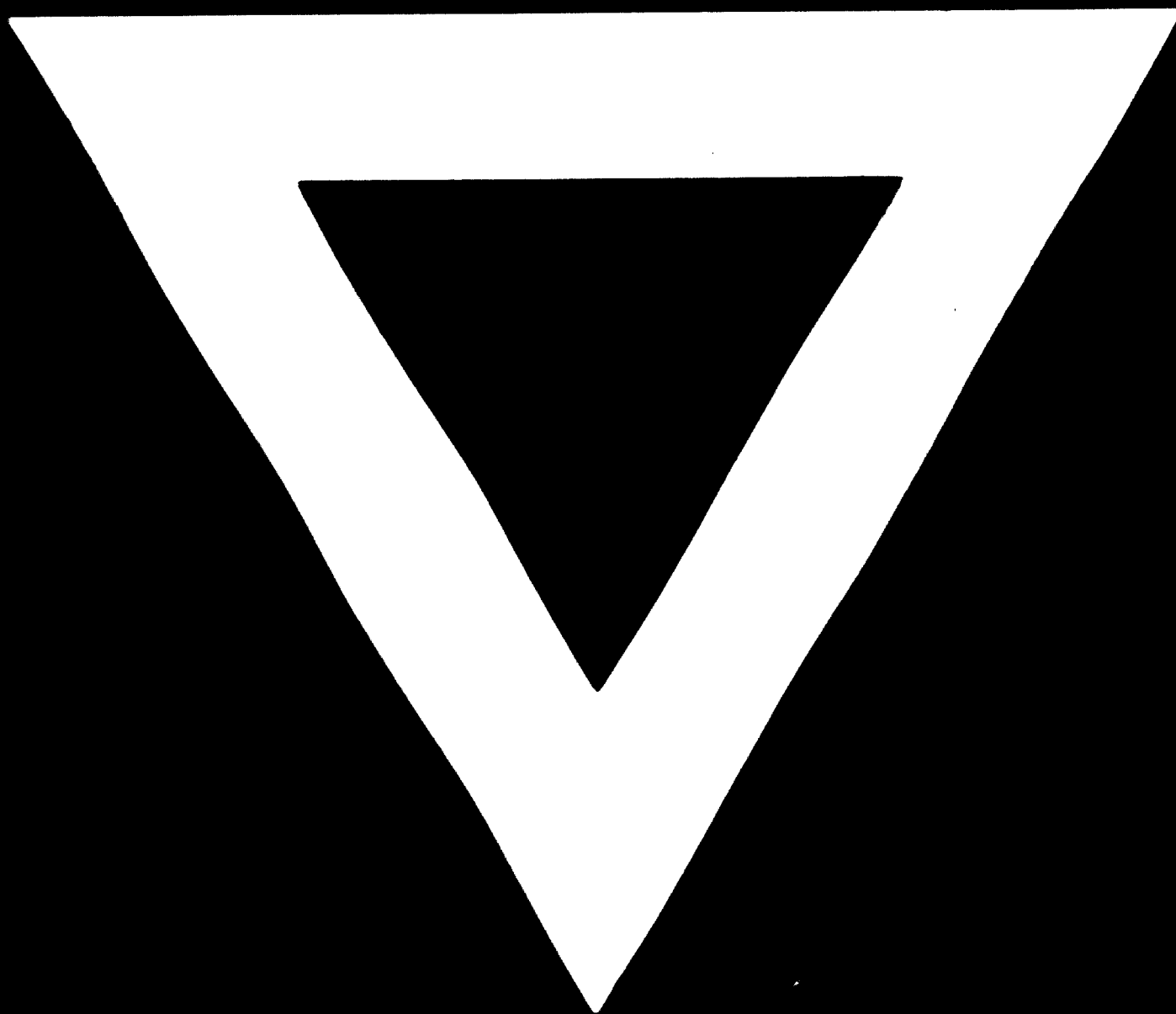37) Bjorksten Research Laboratories. Reports to Sugar Research
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