POLYTERPENE RESINS: Part I – A Brief Historical Review

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Abstract: The terpenic resins are polymers of low molecular weight hydrocarbons, obtained by cationic polymerization of terpenes. These products are used in the adhesives, sealants and wax coating industries.

Commercial adhesive resins are prepared from monoterpenes - the main ones are α-pinene, β-pinene and dipentene.

The softening point and molecular weight of polyterpene resins are critical for their main use (adherence).

Its adhesive behavior results from the relationship of the softening point with the molecular weight.

At the commercial level, polyterpene resins are produced by polymerization of terpene monomers. Batch and continuous systems are used.

The composition of an adhesive requires a wide knowledge of the materials available and the specific requirements of its application.

The most common types of adhesives are Pressure Sensitive Adhesives, Hot-melt Adhesives and Structural Adhesives.
Key words: Turpentine; derivates; production; chemistry; physical properties; applications; types of Adhesives

RESINAS DE POLITERPENOS: Parte I – Uma Breve Revisão Histórica
Sumário. As resinas terpénicas são polímeros de hidrocarbonetos de baixo peso molecular, são obtidas pela polimerização catiónica de terpenos. Estes produtos são usados nas indústrias de adesivos, vedantes e ceras de revestimento.

As resinas adesivas comerciais são preparadas a partir dos monoterpenos - os principais são o α-pineno, β-pineno e dipenteno.

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O ponto de amolecimento e o peso molecular das resinas de politerpenos são críticos para a sua principal utilização (aderência). O seu comportamento adesivo resulta da relação do ponto amolecimento com o peso molecular.

A nível comercial as resinas de politerpenos são produzidas por polimerização em solução de monómeros de terpenos. São usados sistemas batch e contínuo.

A composição de um adesivo requer um amplo conhecimento dos materiais disponíveis e dos requisitos específicos da sua aplicação.

Os tipos mais comuns de adesivos são os adesivos por sistemas sensíveis à pressão, adesivos de hot-melt e adesivos estruturais.

Palavras-chave: Aguarrás; derivados; produção; química; propriedades físicas; aplicações; tipos de adesivo

RÉSINES DE POLYTERPÈNE: Partie I - Un Bref Aperçu Historique

Résumé. Les résines terpéniques sont des polymères d'hydrocarbures de bas poids moléculaire, obtenus par polymérisation cationique de terpènes. Ces produits sont utilisés dans les industries des adhésifs, des mastics et des cires de revêtement.

Les résines adhésives commerciales sont préparées à partir de monoterpènes - les principaux sont l'α-pinène, le β-pinène et le dipentènes.

Le point de ramollissement et le poids moléculaire des résines de polyterpène sont essentiels pour leur utilisation principale (adhérence). Son comportement adhésif résulte de la relation du point de ramollissement avec le poids moléculaire.

Au niveau commercial, les résines de polyterpène sont produites par polymérisation dans une solution de monomères terpéniques. Des systèmes discontinus et continus sont utilisés.

La composition d'un adhésif nécessite une large connaissance des matériaux disponibles et des exigences spécifiques de son application.

Les types d'adhésifs les plus courants sont les adhésifs sensibles à la pression, les adhésifs thermofusibles et les adhésifs structuraux.

Mos-clés: Essence de térébenthine ; dérives ; production ; chimie ; propriétés physiques ; applications ; types d'adhésifs

Introduction

The adhesives are used to join two or more pieces through the contact surfaces. They are classified into:

- Pressure Sensitive Adhesives – PSA;
- Hot-melt Adhesives;
- Structural Adhesives.

The terpene resins are low molecular weight hydrocarbon polymers prepared by cationic polymerization of terpenes. These products, are used by the adhesives, sealants and wax coating industries.

Chemistry

Commercial tackifying resins are prepared from monoterpenes. The α-pinene, β-pinene and dipentene raw materials are derived from turpentine by fractional distillation. The supply of dipentene can also be obtained from limonene collected - by-product - during processing citrus fruits to frozen concentrate.

α-pinene resins

The α-pinene is the most difficult of the terpenes to polymerize since it does not possess an exocyclic methylene group. It easily forms the same initial carbenium ion as β-pinene and can attack a second α-pinene. The propagation step to trimer (Figure 1) is extremely difficult for steric reasons.
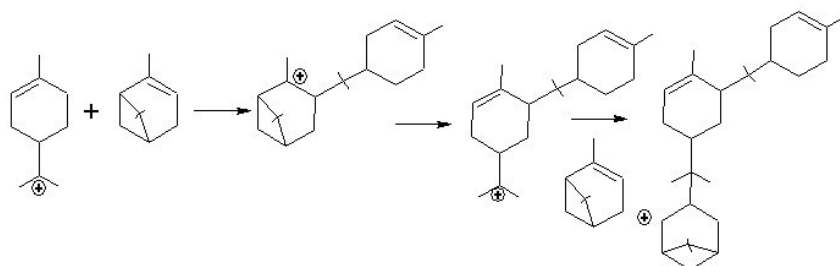

Figure 1 - Polymerization of α-pinene

The presence of an adjuvant (BARKLEY, 1969; RUCKEL, 1977 and 1978; WANG, 1977; WOJCIK, 1977 and 1977a) is required to eliminate the formation of large amounts of dimer, which otherwise would be the main product of polymerization. It is presence of the adjuvant such as $SbCl_3$ (antimony trichloride) is thought to stabilize the growing carbenium ion, providing a longer lifetime, during which it can attack another α-pinene monomer. Chain transfer is suppressed and the polymer forms.

The peracid oxidation of α-pinene resins shows that approximately two-thirds of the mer units contain an olefin indicating that in the remaining one-third, the four-membered ring must expand and result in a saturated mer unit having the bicyclic system. Therefore, the two most probable mer structures A and B in an α-pinene resin are illustrated in Figure 2. (PESTANA DA SILVA, 1991)
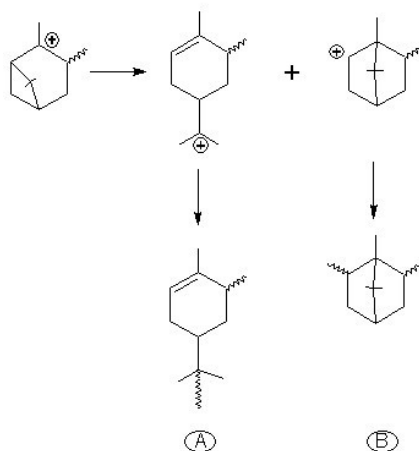

Figure 2 - Structural units of α-pinene resin

β-pinene resins

The actual catalyst for polymerization of terpenes is a complex protonic acid, derived by the interaction of a Lewis acid, usually $AlCl_3$, as a catalyst or promoter such as adventitious water. The initiation step is concluded when the produced proton attacks the exocyclic methylene group of a β-pinene monomer (Figure 3). (PESTANA DA SILVA, 1991)
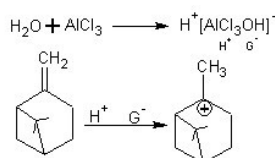
Figure 3 – Initial step of β-pinene polymerization

The tertiary carbenium ion rearranges prior to its attack on another monomer which begins the propagation process (Figure 4). (PESTANA DA SILVA, 1991)
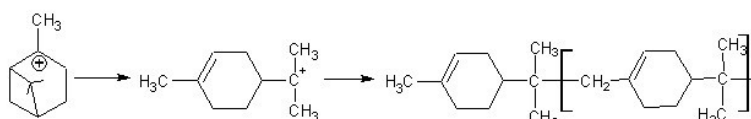

Figure 4 - Propagation of β-pinene polymerization

The main repeating unit in a β-pinene resin is a disubstituted hexane cycle. Theoretically, this resin can be seen as a perfect alternating copolymer of isobutylene and cyclohexane and its chemistry can be explained on that basis. These resins have relatively low molecular weight (ROBERTS, 1950). Figure 5 shows the transfer that occurs during the reaction, through rearrangements of a bicyclic system and the loss of a proton to form a camphene end group. The camphene carbenium ion is non-propagative for stereic reasons. (TAKATA, 1966)
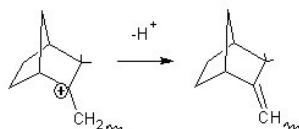

Figure 5 - Camphene end group on β-pinene polymer by rearrangement

A minor chain transfer step to solvent also occurs during its commercial production. Here aromatic solvents are used because of safety and reactivity reasons. The most commonly used solvent is mixed xylenes. In this case, the

growing end attacks the solvent with the elimination of a proton to produce the end group shown in Figure 6. (PESTANA DA SILVA, 1991)
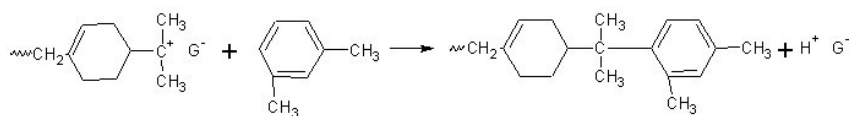

Figure 6 - Chain transfer to solvent during terpene polymerization

Dipentenic resins

The initiation step is similar to what was previously described for β-pinene resins. The proton initially attacks the easily available exocyclic double bond. Propagation proceeds with the carbenium ion attack on the exocyclic double bond of another monomer to result in the structure shown in Figure 7 (PESTANA DA SILVA, 1991)
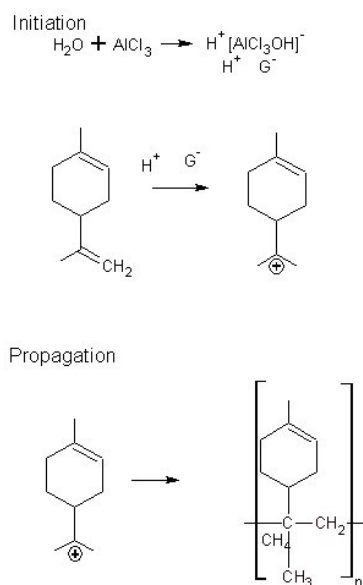

Figure 7 - Dipentene polymerization

However, it is known that only one-half of the mer units have the expected unsaturation. To explain this, the ring double bond must be involved in the polymerization and be consumed during the process. It is speculated that the dipentene polymerization might proceed by initiation at the tri-substituted ring position with the carbenium ion undergoing cyclic polymerization to yield a structural unit as shown in Figure 8. (PESTANA DA SILVA, 1991)
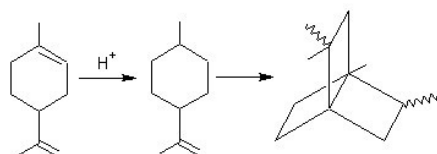

Figure 8 - One possible propagation route for dipentene polymerization (BUTLER, 1965)

Terpene phenolics

The terpene phenolic resins are generally produced by boron trifluoride catalyst of a substituted phenol and a terpene (GOBRAN, 1975 and 1977). Often other dienes are added. The useful resins produced have low molecular weights and softening points somewhat in excess of the polyterpene resins. Because of the phenolic component, they are usually used to stick adhesive system to polar substrates or are used in polar elastomer systems.

Hydrocarbon modified polyterpene resins

It is possible to prepare several modified polyterpene resins by mixing a hydrocarbon monomer such as styrenes with the terpene. The polymerization sequence is also a cationic polymerization. These modified polyterpene resins have properties which are a mixture of the hydrocarbon modifier and the terpene, and find specific uses according to the adhesive composition. (ZINKEL, 1989)

Physical properties

The softening point and the molecular weight of polyterpene resins are critical for their major use as tackifiers for adhesive formulations (RUCKEL, 1975), as these properties may be correlated to utility.

To develop this relationship, it must be understood that hot melt and PSA are formulated from a high molecular weight polymer (rubbery, non-tacky) and a low molecular weight tackifier resin (a brittle glass). The high polymer contributes strength through crystallites or entanglements of extremely long chains and reinforcement by double bonds whereas the terpene resin, with its low molecular weight, acts as a solid solvent and induces a rapid change in viscosity with temperature, allowing wetting of the required substrate of an adhesive.

The adhesive behavior will be more effective when the softening point versus molecular weight curve begins to level for a horizontal asymptote (Figure 9), taking on a transparent amber glass.

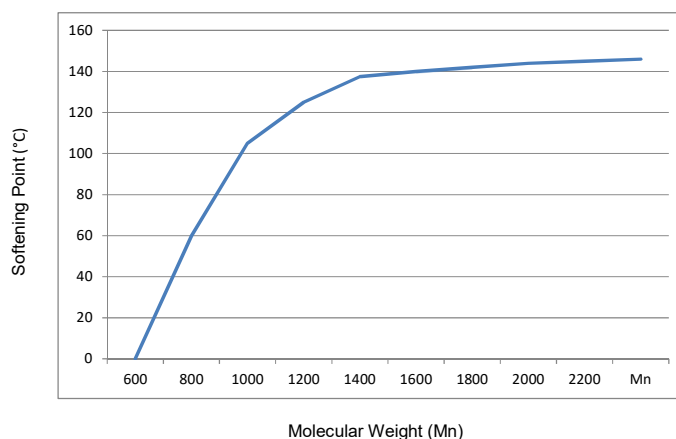

Figure 9 - Effect of molecular weight on softening point of β-pinene resin (ZINKEL, 1989)

For a specified softening point, dipentene and α-pinene resins have lower molecular weight than a β-pinene resin, indicating that the dipentene and α-pinene resin structures are more rigid and more compact than β-pinene. The density of dipentene resins is higher than β-pinene resins (0.998 to 0.974)

corroborating the presence of rigid fused ring moieties. Although dipentene resins have a higher softening point, they have a lower volume than β-pinene resins and hence form solutions of lower viscosity. The pseudo cross-linked nature is also demonstrated by greater thermal stability in comparison to β-pinene resins.

The density of α-pinene resins (0.976) is very close to that of β-pinene resins but, more important, the molecular weight and volume are closer to those of dipentene resins than β-pinene. For this reason, the bulk properties of α-pinene resins are resenable thosee of dipentene resins than β-pinene, with the exception of thermal stability. The thermal stability of a resins is poor because of the partial steric interaction owing to the disubstituted cyclohexane ring and absence of any crosslinks. The structural characteristics of each resin determines the specific adhesive use area. (ZINKEL, 1989)

Commercial production

Polyterpene resins are produced commercially by solution polymerization of terpene monomers. Batch and continuous systems are used. In a continuous reactor, the terpene monomer, aromatic solvent and catalyst are metered into a stirred reactor. About 100 parts of each monomer and solvent are employed, with two or more parts of catalyst. The elegible catalyst for this cationic process is powdered $AlCl_3$, which is constantly metered into the stirred reactor. Since a large exotherm occurs during the polymerization, the component feed rates and cooling are adjusted to keep the temperature within a set interval, usually ranged between 30 and 60°C. (ZINKEL, 1989)

In the continuous system, the polymerization mixture is continuously pumped into a secondary reactor, where the remaining 10% or so of the reaction is completed. The catalyst is subsequently deactivated by adding a turbulent water stream to the polymerization mixture, following which the organic phase is separated. A variety of modified catalyst quench systems are used, but they do not change the quality of the resin. After further washing to remove residual inorganic catalyst remnants, the solvent solution of resin is dried and enters the workup stage. The resin can be recovered either by batch or continuous processing. In batch process reaction, solvent is distilled from the resin solution, gradually increasing the temperature to about 230°C, with the application of vacuum during the final stage. The base resin softening point (DEWALT, 1970) is generally about 110°C and can be adjusted upward to 135°C

by subjecting the molten resin to steam sparging. This technique removes traces of solvent and part or all of the lower molecular weight dimers and trimers present.

The workup of the resin solution can also be accomplished using continuous stripping units. In this case, the precise resin softening point can be obtained directly by the judicious choice of time/temperature variables. (ZINKEL, 1989)

Adhesive applications

Adhesive components

The softening points and molecular weight of the polyterpene tackifier resin are critical for their major use in adhesive formulations. The cyclic and polycyclic structure results in high softening points at low molecular weight and excellent dissolving power for elastomers and, also, the stability of these resins against oxidation, lead to the best tackifier resin choice for producing adhesives.

The adhesives produced from the various terpenic resins consists of two main components - tackifier resin and polymer or elastomer. A variety of minor components are also used to stabilize the system and slightly modify the adhesive properties. (ZINKEL, 1989)

Coatings and some hot-melt sealants prepared from these terpene resins are composed of tackifier resin, polymer and wax in roughly equivalent amounts. The wax component reduces costs, reduces moisture vapor transmission and protect coated surfaces from the aggression effects by external agents (physical, chemical, etc.) and improves coatability.

The major polymers used are natural rubber, synthetic rubber, block elastomers and ethylene-vinyl acetate copolymer. When specific adhesive properties are required, specially polymers are employed. As the chemical compositions and the solubility parameters of these polymers broaden, the composition of the tackifier should be redesigned to provide useful systems.

Most adhesive systems contain 1 to 10% of other additives which fall into categories of stabilizers or adhesive property modifiers. Examples of stabilizers are phenolic antioxidants, phosphite antioxidants and ultraviolet stabilizers. Adhesive property modifiers are typically oils, reinforcing resins and/or waxes to modify cold temperature properties, high temperatures shear and moisture

vapor transmission. Small amounts of fillers are used to color, opacify or stiffen adhesives. (ZINKEL, 1989)

Adhesive properties

Compounding an adhesive requires a broad knowledge of the materials available and the requirements of the specific adhesive application. Adhesive properties are measured by their ability to wet a substrate (tack), the ease of removal by peeling (peel) and their cohesive strength (shear).

The primary importance is the ability of a formulation to wet a surface, so that intimate and complete contact with the substrate is possible. When this has occurred, the hydrogen bonding and Van der Waals' forces can provide the desired bond between substrate and adhesive.

Functionally, it is not possible for a high polymer, such as rubber or ethylene vinyl acetate, to wet a substrate without extreme pressure due to the limited segmental motion of the long chain. When a tackifier resin is added (this with low molecular weight), it acts as a solvent (DEWALT, 1970) and enhances segmental motion, so that the segments of the long polymer chain can easily wet the substrate with little or no pressure. This property, derived from tackifier, allows a polymer-tackifier mixture to become an adhesive. It is called tack.

Once stuck to a surface, the adhesive must resist removal by peel and the removal of a flexible substrate, such as tape, from a rigid surface by pulling at a 90° to 180° angle to the rigid substrate. Here the adhesive fails at a thin bond line. Peel values will be designed to be high or low depending on the needs of the application.

The third property of an adhesive is its cohesive strength. This is the interior strength of the adhesive generated by the polymer through chain entanglements, crosslinks and crystallites. If the adhesive has high cohesive strength, it will fail adhesively at the bond line or in extreme cases will cause a failure of the substrate surface (fiber tear).

These three characteristics must be formulated into the adhesive, to give the desired adhesive properties, and then must be stabilized so that the formulation will perform for the required period under the desirable environmental conditions. (ZINKEL, 1989)

Common types of adhesives

Pressure Sensitive Adhesives – PSA

These adhesives are made up of complex mixtures of polymers and copolymers (blocks), adhesive resins, stabilizers, reinforcement/filler loads, etc., and the tackifier (tack) to the substrate does not require activation by solvent, heat or humidity. Instant tackiness is strongly correlated with the viscoelastic behavior of these systems. The oldest contact adhesives have been used solvents (as gum arabic), or natural rubber latex. Currently, reasonable sophisticated formulations are used based on acrylics, synthetic elastomers - styrene-butadiene copolymers (SBR or SBS) -, silicones, emulsions, etc..

In this group there are three types of adhesives according to their method of application: solvent applied, hot melt applied and waterborne.

The classic solvent-based adhesives consisted of milled natural rubber and tackifier dissolved in aromatic solvent at about 12-15% solids. Industry uses three routes to maintain viable economics: higher solids solutions, hot-melt systems and waterborne systems. Each of these has advantages and disadvantages.

Recent technology (HOLDEN, 1984; JOHNSON, 1985; LEGGE, 1983) is leaning towards production of PSA by hot-melt extrusion methods. This was become possible with the advent of the thermoplastic block elastomers, which generally are composed by three commercial blocks, i.e., styrene-isopropene-styrene or styrene-butadiene-styrene. These relatively low molecular weight materials, when heated above the transition point for the styrene domains, are thermoplastic; their viscosity drops and mixing is possible. The molten formulation can then be extruded onto a substrate. On cooling the formulation, the styrene domains reform producing a PSA with excellent shear properties. (ZINKEL, 1989)

The performance of this type of adhesives depends on:
- The composition of the base chain in terms of the selected monomers;
- The features that incorporate the base chain;
- Of molar mass and degree of branching of polymer chains;
- The number, type and functionality of the chain branches;
- The possible presence of interpenetrating polymer networks (IPN);
- The formulation in terms of secondary components (as plasticizers).

Hot-melt adhesives

Hot-melt adhesives are essentially made of thermoplastics with a melting point above 120ºC. The mechanical strength of the joint occurs after cooling.

The hot-melt formulations are separated into hot-melt adhesives, which form their bond on cooling, and hot-melt coating which are applied as a continuous film, usually on a flexible web or substrate (paper or plastic).

Hot-melt adhesives produced in largest quantities are those for sealing packaging and cartons. These materials are generally a mixture of resin, elastomer and often wax. The most used elastomers are ethylene vinyl acetate and thermoplastic block copolymers.

The typical formulation of a hot-melt adhesive includes:

• Basic thermoplastic (largely major component);
• Tackifying resins by adding oligomers to control surface tension (wetting of substrates), improving both instant tack and peel resistance;
• Plasticizers/thinners to reduce the temperature of the glass relaxation and control the melt viscosity, at the same time. Incidentally they also modify the surface tension (wetting);
• Waxes to control the speed of application of the adhesive and increase the hardening cycle;
• Anti-oxidants.

These are predominantly ethylene-vinyl acetate mixtures with the tackifier and wax, suitable for coating paper, plastic and presenting a good final appearance, providing a moisture barrier. An example is the sealable coatings on freezer food packages. (ZINKEL, 1989)

Structural adhesives

Structural Adhesives are essentially made up of formulations of different monomers or oligomers that polymerize *in-situ* (hardening, curing) giving rise to a very tight three-dimensional polymer.

There are systems with:

• Two components (resin and polyfunctional hardener) in which the components are mixed before application, and react chemically with each other (thermosetting);
• One-component (polyfunctional resin) in which crosslinking is induced by the action of UV/VIS radiation (photosensitive resin), by reaction with

atmospheric oxygen (e.g. cyanoacrylates) or atmospheric moisture (e.g. polyurethanes).

The most used resin are epoxy resins, acrylic resins and urethanes.

Construction adhesives

There is a wide variety of materials used for these applications, mainly because of the varied requirements of the applications. Construction adhesives are used to lay floors tile, cement light weight interior ceiling tilles, for decorative walls laminates and to provide squeak-proof floors. Many of these applications require a substantial gap filling ability; consequently, many of these materials contain large percentages of fillers. (ZINKEL, 1989)

Sealants

Sealants are used to isolate and prevent the passage of fluids (gas, liquid) across the border of the sealed region. They consist essentially of elastomer formulations, which are generally complex with 15-30 components.

This category of adhesives has the highest environmental performance standards of any of the adhesives presented. By their very nature, they must often stand up to ultraviolet light and extremes of temperature in external building applications. Their long-term stability is of critical importance. (ZINKEL, 1989)

References

BARKLEY, L.B., PATELLIS, A.P.U.S., 1969. Patent 3,478,007.

BUTLER, G.B.; MILLES, M.L.; BRAY, W.S., 1965. *Journal of Polymer Science* Part A, 3, p. 723.

DEWALT, C., 1970. *Adhesives Age* **13** (3):38.

GOBRAN, R.U.S., 1975. Patent 3,927,239.

GOBRAN, R.U.S., 1977. Patent 4,032,486.

HOLDEN, G., ST. CLAIR, D.J., 1984. *Proceedings TAPPI Hot-melt Short Course,* pp. 31-40.

JOHNSON, K.E., 1985. *Adhesives Age* **23**(12): 29.

LEGGE, N.R., 1983. COHENTech **13**: 630.

PESTANA DA SILVA, M.M.N., 1991. *Aguarrás - Aplicações Industriais*, LNETI - Laboratório Nacional de Engenharia e Tecnologia Industrial.

ROBERTS, W.J., DAY, A.R., 1950. *Journal of the American Chemical Society* **72**: 1226.

RUCKEL, E.R.; ARLT JR., H.G., WOJCIK, R.T., 1975. *Adhesion Science and Technology,* Vol. 9ª, L. H. Lee, ed.,Plemum Press, New York, p. 408.

RUCKEL, E.R.; WANG, L.S.U.S., 1977. Patent 4,057,682.

RUCKEL, E.R.; WANG, L.S.U.S., 1978. Patent 4,113,653.

TAKATA, A., OTSU, T., TIMOTO, M., 1966. *Kogyo Kagaku Zasshi (Journal of the Chemical Society of Japan* **69**: 715.

WANG, L.S., RUCKEL, E.R.U.S., 1977. Patent 4,001,385.

WOJCIK, R.T.,RUCKEL, E.R.U.S., 1977. Patent 4,016,346.

WOJCIK, R.T.,RUCKEL, E.R.U.S., 1977. Patent 4,048,095.

ZINKEL, D., RUSSELL, J., 1989. Naval Stores, *Pulp Chemical Association*, New York, pp. 510-530.