Translated from *Uspekhi Khimii*, 52 1196-1224 (1983) U.D.C. 634.0.813.11

Lignins as Components of Polymeric Composite Materials

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The results of studies of natural, native, and technical lignins are surveyed. Data are presented on the structures and physicochemical properties of various technical lignins (hydrolytic, sulphite, and sulphate lignins), which constitute the waste of the cellulose-paper and hydrolytic industries. Considerable attention is devoted to the examination of the properties of lignins which are responsible for their employment for the reinforcement of elastomers and the modification of plastics.
The methods of utilisation and rational employment of technical lignins in the plastics industry as active ingredients of polymeric composite materials are examined.
The importance of sulphate lignins as the most active from the standpoint of structure and properties in relation to the polymer matrix for the creation of highly filled lignin-containing polymeric materials—lignoplastics of the type of poprolin—is specially emphasised.
The bibliography includes 160 references.

CONTENTS

I.	Introduction	675
II.	The chemical structure of the natural lignin macromolecule	676
III.	Industrial methods for the delignification of wood and the properties of technical lignins	677
IV.	Hydrolytic lignin and its utilisation	679
V.	Sulphite lignin (lignosulphonates) and its utilisation	680
VI.	Sulphate alkali lignin (Kraft lignin) and its applications in the modification of polymeric materials	681

I. INTRODUCTION

The accelerated rate of growth of the industry of polymeric materials under the conditions of the world economic crisis, the exhaustion of the petroleum resources, and the deficiency of polymeric raw materials has faced science and industry with new tasks involving the extraction and effective employment of the existing reserves and also the rational utilisation of the available natural resources.

From this standpoint, one of the promising trends in the technology of the processing of polymers is the formation of polymeric blended and highly filled composite materials with high indices of physicomechanical and operational properties. For this reason fillers play a major role in the solution of this important problem[1].

Practical experience has shown that the introduction of low-molecular-weight and high-molecular-weight fillers of different chemical types into the polymer matrix makes it possible to alter specifically the physicomechanical, rheological, and thermophysical characteristics of the polymeric materials and the articles obtained from them[2].

The creation of highly filled polymeric composites containing more than 20% of the filler (by volume), which involves a decrease of the consumption of the scarce basic polymer and a reduction in the cost of the material, is exceptionally important. This requires in its turn the search for cheap mineral and organic fillers the raw materials for which are extensive and readily available.

Calcium carbonate, kaolin, talc, silicon dioxide, metal oxides, asbestos, wollastonite, etc. have come to be widely used as mineral fillers[3-5]. The waste from stone quarries and stone processing industries, namely finely fragmented tuff, is used for this purposes[7].

Among organic fillers, carbon black, cellulose, carbon and graphite fibres, sawdust, cotton, coke, starch, and certain other substances have found applications[5,8].

Lignin and their degradation products[9-11], as well as kerogens and their processing products[12,13], which constitute the waste of the sulphate-cellulose and shale industries, are extremely promising organic fillers.

In selecting the fillers for polymeric materials, preference is given to organic products active in relation to the basic polymer, which facilitates their "combination" and the conversion of the compositions into finished articles and improves their physicomechanical characteristics.

The most widely used organic fillers for polymers are various kinds of carbon black, which still remain of primary importance, particularly in the technical rubber industry, where they are used as agents reinforcing elastomers[9,14]. However, the group of thermoplastic materials, for which readily available fillers of organic origin must be sought, provides the greatest potential possibilities for the development of the manufacture of filled polymers.

Technical lignins, which were first used as reinforcing fillers in natural and cured rubbers[15,16] but which have hitherto found limited applications in the plastics industry, are of great theoretical and practical interest from this standpoint. Admittedly, in view of the deficiency of the primary polymeric raw material, interest in lignin as a filler for thermoplastics has greatly increased in recent years in connection with the possibility of its employment for the creation of composition materials based on thermoplastics and their industrial waste[10,11,17-21].

Lignins are natural organic raw materials, since they are constituents of wood and plants (their content in wood reaches 30%), where they play the role of lining agents[22], and are comparable in this sense to cement and iron concrete[23] (p.259). Thus lignins are one of the high-molecular-weight components of wood and occupy the second place (after cellulose) as regards their abundance throughout the world as organic polymeric substances of natural origin.

Lignins are not only lining materials but also reduce the permeability of cell walls and thereby play an important role in the transport of water, nutrient substances, and metabolic products. They also impart rigidity to the cell walls and, acting as an intercellular binder, impart to wood resistance to impact, compression, and bending. Lignification renders the woody tissue more resistant to the action of microorganisms.

The lignins present in plant tissues are referred to as natural lignins, protolignins, or lignins *in situ*. The term "native lignin" refers to the preparation isolated by Brauns's method[24].

When lignin is isolated from wood (delignification of wood), it undergoes significant chemical changes which depend on the method of isolation so that the lignins obtained under industrial conditions (technical lignins) are not identical in their structure to nature lignins.

Technical lignins constitute the waste of the cellulose-paper and hydrolytic industries and are utilised extremely irrationally—mainly by combustion[25,26]. However, the lack of reliable data concerning the structure of lignin precludes the determination of its behaviour in a polymer matrix and retards its employment as a filler of thermoplastics.

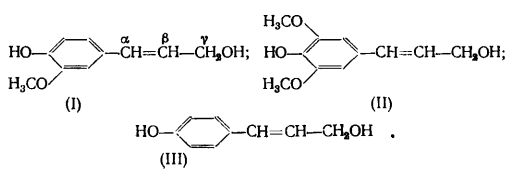
On the other hand, extensive theoretical and practical data have accumulated, which makes it possible to regard lignin as one of the promising fillers and modifying agents for polymeric composites (of the type of poprolin). It is therefore necessary to consider briefly the structure and properties of natural and technical lignins.

II. THE CHEMICAL STRUCTURE OF THE NATURAL LIGNIN MACROMOLCULE

The term "lignin" originates from the Latin word lignum (wood) and does not refer to an individual substance but to a group of related substances having common compositions, structures, and chemical properties for which Freudenberg suggested the term polylignols[27] and Shorygin suggested that they be referred to as lignin substances[28].

Lignin substances should be present in all plant tissues but some investigators hold the view that lignin appears in the course of the evolution of plants only in plants adopting a terrestrial mode of existence and that lignin is absent from seaweed[29].

At the present time lignins are understood as natural polymeric products formed by the enzymic dehydrogenation polymerisation of three main precursors: coniferyl alcohol (I), sinapyl alcohol (II), and *p*-coumaryl alcohol (III):[24]



The lignin macromolecule is formed in this process as a result of the combination of phenoxy-radicals, like other natural phenolic substances. Problems concerning the formation of the precursors of lignin and its biosynthesis in the plant cell walls *in vitro* and its chemical reactions have been described in detail in the literature[22,23,25-28,30-39] and there is therefore no necessity to dwell on them.

One should note that natural lignins undergo appreciable changes even on mild chemical treatment and for this reason methods permitting complete isolation of lignin from plants without the alteration of its chemical structure have not been found hitherto. The problem of obtaining ligning preparations analogous to natural lignin continues to be the most important in the chemistry of lignin.

Natural lignins have a number of specific properties: they are readily oxidised, they readily interact with chlorine, which is an important factor in the bleaching of cellulose, and they are soluble in alkalies on heating. This ability of lignin constitutes the basis of the alkaline delignification of the sulphate and soda methods of manufacture of cellulose, while its ability to dissolve on heating in aqueous solutions of sulphurous acid and its acid salts is used in the delignification of wood by the sulphite method[25].

Lignins are resistant to the hydrolytic action of solutions of inorganic acids and contain a large number of methoxy-groups, which serve as sources of methanol and unpleasantly smelling methyl-substituted sulphur compounds, and also several per cent of phenolic hydroxyls, which play an important role in the modification of thermoplastics[24,25,40].

The ability of lignins to be readily oxidised is used not only in the bleaching of cellulose but also in the preparation of a number of valuable products such as vanillin, vanillic acid, etc.[24,30]

Lignins from different plants differ appreciably in their structure and for this reason one distinguishes (1) conifer wood lignins, (2) deciduous wood lignins, and (3) grassy plant lignins. Conifer wood lignins have been most thoroughly investigated—they form a fairly homogeneous group of substances and even lignins from different conifer species have very similar properties. On the other hand, the lignins from deciduous tress and grassy plants have been less well studied and are distinguished by a wide variety owing to their complex chemical structure[22,24].

In the entire specialist literature on the chemistry of lignin, mention is made of the fact that its structure has been poorly investigated compared with a whole series of other substances with more complex chemical structures such as proteins, various enzymes, etc., which can be explained by the chemical inhomogeneity of the lignin macromolecule and the unsuitability of many classical methods of organic chemistry in the study of its structure. Therefore hitherto there is no formula which corresponds exactly to its real chemical structure.

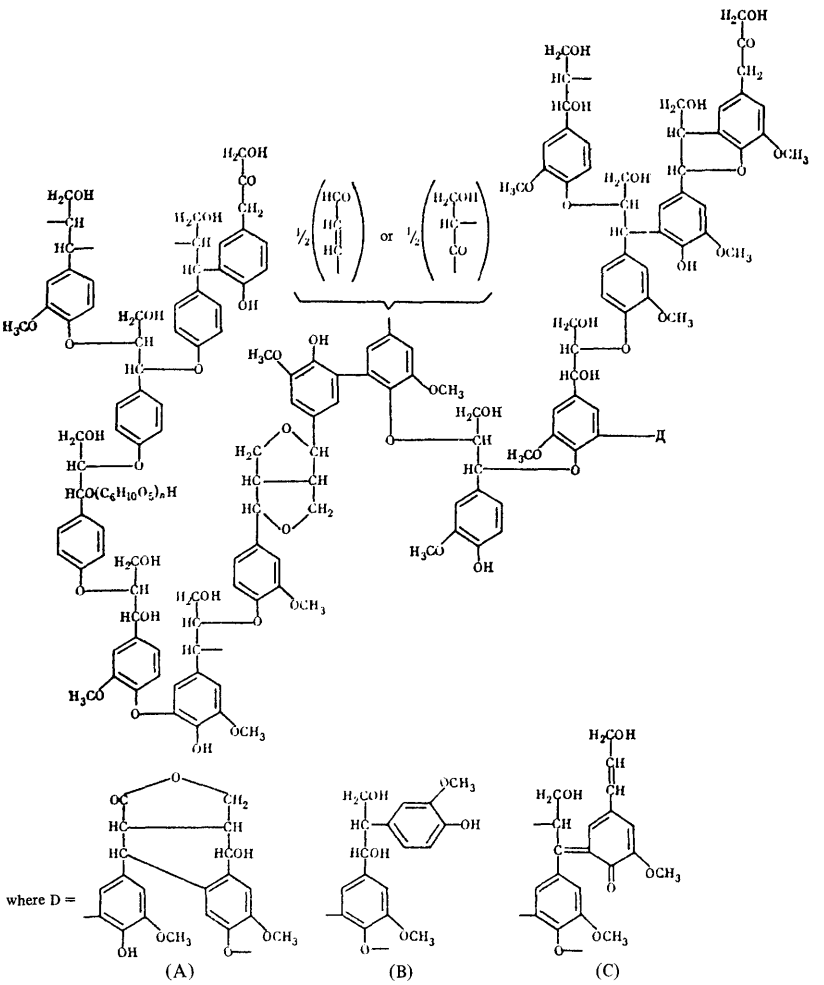
Among all the known hypothetical formulae, reflecting the chemical structure of lignin, that proposed by Freudenberg is believed to be the most successful. A fragment of the molecule of native lignin is presented in Scheme 1,[24] where D represents the possible versions of the dimeric unit (A, B, C).

Adler proposed an ionic mechanism for the biosynthesis of lignin, but here too the initial stage proceeds via a radical mechanism and without electron transfer[34,41], which is of significant interest for the explanation of the character of the interaction of lignin with thermoplastics when it is introduced into the polymer matrix.

Investigators who have studied lignosulphonic acids, which are formed in the bisulphite digestion of Norway spruce, reached an interesting conclusion concerning the structure of the monomeric unit of natural lignin. They subdivide the aromatic compounds of spruce wood into lignin and hemilignin (by analogy with cellulose and hemicellulose) and believe that certain contradictions in the chemistry of lignins are associated with the different contents of hemilignin in the lignin preparations investigated[42,43]. It was shown in these studies that spruce lignin has a high degree of structural homogeneity and is a polymer consisting of identical monomeric units, each of which contains 16 guaiacylpropane and two *p*-hydroxyphenylpropane groups, which corresponds to Freudenberg's structure of lignin and confirms yet again the agreement between Freudenberg's hypothetical formula and the real structure of lignin.

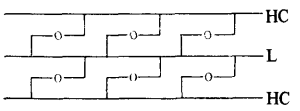
Data concerning the structure of lignin *in vitro* permit the next step—the elucidation of its "secondary" structure in plants (*in vivo*) taking into account the polymers surrounding lignin in wood, which have different compositions and structures[40,44].

Scheme 1



As pointed out by a number of investigators, lignin exists in plant tissue as a carbohydrate complex and is linked to the cellulose and hemicelluloses in wood, mainly via an oxygen bridge[30,45–47]. Lignin bound to hemicelluloses, namely hemilignin, must have a branched structure. The relative distribution of hemilignin (L) and hemicelluloses (HC) in wood is represented in Scheme 2 taking into account the lignocarbohydrate linkages[40].

Scheme 2



The molecular weight (MW) of natural lignins is comparatively high (of the order of several thousands, but is lower than that of technical lignins); they have a fairly porous structure and a large specific surface (the specific surface of native lignin is 180–280 $m^2\ g^{-1}$).[22]

Thus natural lignin has a fairly high molecular weight and is located in wood between cellulose fibrils and is therefore accessible to the action of reagents only after the hydrolysis of the cellulose or the loosening of the fibrils with rupture of hydrogen bonds. The delignification of wood under industrial conditions and the preparation of technical lignins are based on this principle[22,25,26].

III. INDUSTRIAL METHODS FOR THE DELIGNIFICATION OF WOOD AND THE PROPERTIES OF TECHNICAL LIGNINS

The methods for the isolation of lignin from wood and other plant materials are based either on the dissolution of the carbohydrates present in wood and the preparation of lignin in the form of an insoluble precipitate (in the preparation of hydrolytic lignin) or on the dissolution of lignin with its subsequent precipitation (in the preparation of alkaline lignins and lignosulphonates)[22,25,48].

Three methods of processing wood are used in the USSR and the side products of these industries are various technical lignins.

1. By a hydrolytic procedure, in which wood is treated with a dilute solution of sulphuric acid, hydrolytic lignin being obtained in the form of a non-hydrolysable residue[25].

2. By the sulphite method, in which wood is treated with a solution of calcium, magnesium, or ammonium bisulphite and

sulphurous acid, sulphite lignin or lignosulphonates being obtained[25].

3. By the sulphate method, in which wood is treated with a solution of caustic soda and sodium sulphide with formation of alkali lignins (sulphate alkali or soda alkali methods depending on which reagent is used to make good the loss of alkali)[48].

In conjunction with modern technology, the sulphate method is the most economical (compared with the soda method) since the chemical reagents are regenerated in a closed system with a high technical efficiency, which makes it possible to eliminate completely the pollution of soil and water reservoirs. These advantages of the sulphate method of the manufacture of cellulose explain its vigorous development both in the USSR and abroad, where sulphate lignin is known mainly as Kraft lignin[22,48].

Sulphate lignins have the highest chemical reactivity compared with other technical lignins.

The structure and properties of technical lignins depend on the type of tree from which the wood has been obtained and the method of its treatment, i.e. are determined by the type of digestion process.

Like native lignins, technical lignins are polyfunctional high-molecular-weight aromatic compounds made up of phenylpropane structural units whose characteristic feature is an irregularity of structure and a wide variety of linkages; their density is in the range 1330–1450 kg m^3 and they have high specific surfaces (from several units to several hundreds of $m^2\ g^{-1}$ depending on the moisture content of the product) and a high refractive index (1.61) as a consequence of their aromatic nature[32]. The difference between the structures of technical and natural lignins are indicated by the results obtained in their investigation and the invstigation of model lignin compounds by physical methods[45,49–60]. The EPR method, which helps to elucidate the mechanism of the modifying action of lignin on thermoplastics in the formation of polymeric composites such as poprolin and lignoplastics, has acquired considerable importance in recent times[61–67].

The first studies designed to detect free radicals (R) in lignin by EPR date back to 1960.[52] The absence of a signal from specimens in the form of fresh dry undamaged wood filings from several trees was reported and the concept of the absence of R in natural lignins was adopted. As a result of the employment of a more sensitive EPR spectrometer, such signals were later detected in undamaged wood of black spruce[53]. It was then observed that the intensity of the EPR signal increases in pulped wood after mechanical treatment and that the intensity of the signal in technical lignins depends on the delignification conditions[53–56].

The results led to the hypothesis that the radicals R are formed as a consequence of the comminution of the rigid lignin network due to the mechanical or thermal degradation in the course of digestion at 180–190 °C and that R should be present in all technical lignins. In all the lignins investigated (regardless of the method of delignification) the EPR signals did not exhibit an appreciable hyperfine splitting. It was found that the lignins from deciduous and conifer wood contain approximately 10^{18} spins per gramme with g-factors of approximately 2.00.[24] The factor $g = 2.00$ confirms that the source of signals in lignins are the radicals R formed on degradation of the lignins and consist of molecular fragments with radical centres having a specific structure[56]. The nature of these paramagnetic centres has not been established but it is believed that they are radicals of the semiquinonoid type. Stable phenoxy-radicals have also been detected, which can be attributed to the dehydrogenation of lignins[57].

Questions involving the study of the free-radical processes in the delignification of wood are important both for a more accurate determination of the structure of lignin and for the explanation of the mechanism of its action when it is introduced into a polymer matrix as an active ingredient of the polymer composition.

These reactions have been studied in greatest detail for sulphate alkali lignin; the results of these studies are examined in the next section.

The thermal properties of technical lignins are significant for their employment in the preparation of polymeric composites because the latter are processed at temperatures in excess of 200 °C. Unfortunately, the existing fairly extensive information in the literature[24,68–73] does not provide an unambiguous answer to the question of the thermal stability of lignins in general and technical lignins in particular, which can evidently be accounted for by objective difficulties which hinder the determination of their exact chemical structure.

The available data on the thermal degradation of lignins indicate their different thermal stabilities, which are determined both by the kind of tree from which the wood has been obtained and by the delignification method[68,69]. It has been established that the lignin obtained from spruce wood has a higher thermal stability, regardless of the method of its isolation, than deciduous lignin; this is caused by the enhanced capacity for condensation processes in coniferous lignin as a result of the accumulation of C–C bonds at high temperatures. There are data showing that lignins are pyrolysed by a free-radical mechanism[105].

It has been shown that the methoxy-groups have the highest thermal stability in the lignin molecule, being retained on heating above 350 °C, and it is therefore to be expected that methoxylation is one of the effective methods for the retardation of the rupture of the alkyl–aryl ether linkages, whose thermal stability is lowest.

Methylation of lignins inhibits the dissociation of the alkyl–aryl ether linkage and not only does not increase but actually somewhat diminishes the overall thermal stability of lignin. The reason for this is that the stabilising effect of the methoxy-group introduced is swamped by the reduction of the number of C–C bonds as a consequence of the cessation under these conditions of the primary condensation process and the decrease of the capacity of lignin for secondary condensation[69], since two competing processes take place in it during heat treatment (at temperatures of 150–300 °C): primary condensation with participation of the hydroxy-groups of the propane chain and the formation of the C–C bonds between the structural units of lignin and the disruption of the weakest alkyl–aryl ether linkages.

Thermographic studies of technical lignins have shown that their thermal stability is not as high as has come to be believed. The temperature range of the softening (glass formation) of lignins varies within wide limits (from 120° to 250 °C) and depends on the method of isolation, the molecular weight, and the moisture content. For example, the glass point of dry native lignin is T_g = 130 °C and that of moist lignin is 50 °C.[24,30]

The structural changes in sulphate lignins due to the softening and compaction of macromolecules are observed already at 150 °C and above and the temperature range 240–360 °C is the region of active thermal decomposition, which takes place with a sharp increase in the number of paramagnetic centres via a free-radical mechanism[74].

It has been noted that the thermolysis of lignins takes place in two stages. The first stage, which occurs at comparatively low temperatures (100–250 °C), involves dehydration; the second high-temperature stage (250–350 °C) proceeds via a radical mechanism[71,74]. Under these conditions, even in a high vacuum and at a low rate of heating the weight loss in the first stage is more than 40% and that in the second is 12%.

IV. HYDROLYTIC LIGNIN AND ITS UTILISATION

Hydrolytic lignin (HL) is a waste product of the hydrolytic industry, which exists only in the USSR, and also of the processing of agricultural waste. When the entire capacity of the hydrolytic industry is utilised, more than one million tons of HL will accumulate annually in the waste. The solution of the problem of the utilisation of such waste is therefore urgently required.

Wood and agricultural plant waste are hydrolysed in special apparatus by percolating a hot 0.5–1% solution of sulphuric acid through a layer of hydrolysable material at 180–185 °C and pressures up to 144 mN m^{-2}.

Hydrolytic lignin is a polydisperse product with a particle size up to 1 cm and is a blend of substances of different chemical types. It incorporates comminuted polymerised lignin proper, polysaccharide residues, monosaccharides which were not washed off in hydrolysis, inorganic and organic acids, resins, waxes, nitrogen-containing substances, and ash elements[25]. In addition, it contains traces of furfural or hydroxymethylfurfural and its structure is that of a cross-linked polymeric product whose molecular weight as well as its chemical structure have not been accurately determined; HL is insoluble in organic solvents, alkalies, and acids.

Hydroltyic lignin is a hygroscopic product, so the moist lignin must be regarded as a three-phase system consisting of solid HL proper, water, and air[25,26,75].

Technical HL obtained in factories is usually highly contaminated by various impurities and its chemical structure varies, which greatly hinders its processing and utilisation both as a reinforcing agent and filler for plastics and elastomers[25,26].

Since HL has a cross-linked structure, it must be improved and modified before being introduced into polymeric materials. The modification of hydrolytic lignin consists in its treatment with active chemical reagents followed by nitration, sulphonation, phosphorylation, chlorination, and certain other reactions. Chlorination is regarded as one of the promising methods for its modification[76].

A number of realistic methods for the activation of HL involves the treatment with alkalies of its aqueous solutions at elevated temperatures (180–200 °C).[26] The mechanism of this process is not yet sufficiently clear, but there exists the view that the dissolution of lignin on treatment with an aqueous solution of alkali takes place as a result of the rupture of ether linkages with loss of methoxy-groups and the formation of free phenolic hydroxy-groups. At the same time the side chains are partly oxidised to carboxy-groups. Alkaline HL is a reactive product and can be used successfully for the reinforcement of elastomers together with sulphate alkali lignin.

Since, as stated above, HL is extremely hygroscopic, its internal surface area is determined by the moisture content (it is 760–790 $m^2\ g^{-1}$ for moist lignin and only 6 $m^2\ g^{-1}$ for dry lignin). The moisture content also determines the specific gravity and bulk density of lignin, which amount to 1500 and 200 kg m^{-3} for the dry product, the specific gravity of the product with 15% moisture content is 1300 kg m^{-3}, and the specific gravity and bulk density of the products with a 65% moisture content are 1150 and 700 kg m^{-3} respectively[77]. The angle of the slope of repose for crude lignin is 40–43°.

Hydrolytic lignin has a porous structure (the pore radius reaches from 30 to 200 Å) and has a low bulk density in the dry state, which reaches 190–220 kg cm^{-3}.

Since HL contains an increased amount of moisture as a consequence of its hygroscopicity and is a coarsely disperse system with a particle size up to 1 cm, before its utilisation it must be subjected to an additional treatment to increase the degree of its dispersion, which is achieved by additional drying, vibromilling, etc. The structural-mechanical (rheological) properties of HL and its capacity to absorb moisture are important for a theoretical justification of the rational drying regimes.

The study of the rheological properties of HL subjected to different degrees of processing and with different moisture contents showed that the general postulates of the physicochemical mechanics of disperse structures can be applied to it[75].

The methods for the utilisation of HL available at present cannot be regarded as rational and scientifically well founded. One of the simplest procedures for its utilisation involves combustion, since the industrial product is highly contaminated by non-lignin impurities and has a cross-linked structure, which creates additional difficulties in its employment. However, moist HL has a low heat generating capacity, which is 5500–6500 cal kg^{-1} for absolutely dry lignin, 4400–4800 cal kg^{-1} for the product with an 18–25% moisture content, and 1500–1650 cal kg^{-1} for lignin with a 65% moisture content, so that its employment as a fuel is ineffective. The low caloric value of HL as a fuel can be explained by the fact that lignin ejected from the hydrolytic apparatus has a moisture content in excess of 90%, so that for each tonne of lignin it is necessary to remove 900 kg of water and this requires a large amount of heat. The drying of lignin is also complicated by the fact that, like cellulose, it can form hydrates with water–lignin-OH.[77]

There exist also other methods for the utilisation of hydrolytic lignin although not on an industrial scale. For example, HL can be used to prepare high-quality brands of activated charcoal. There exist technological schemes which make it possible to obtain charcoal and also other products of the dry distillation of HL. The charcoal obtained is used to manufacture carbon disulphide and carbon tetrachloride, for the preparation of activated charcoal, and also in the manufacture of polymeric materials[25,26,78,79].

More promising ways of using HL involve its chemical reactions.

The oxidative hydrolytic cleavage of HL in an alkaline medium leads to the formation of a mixture of organic acids, which can be used in the yeast industry in the accumulation of the protein and yeast mass, which makes it possible to increase the yeast resources by 20%.[80,81]

The HL nitration products can be used in the drilling for petroleum and gas as substances which reduce the viscosity of clay solutions and the products of nitration with more concentrated (30%) acid can be employed as growth substances[79].

The most promising products are chlorinated hydrolytic lignins which have found applications as substitutes for natural tanning agents and as reinforcing agents for natural rubbers and their activities are similar to those of sulphate lignins[82].

The hydrogenolysis of HL yields between 60 and 85% of low-molecular-weight ether-soluble products which include up to 70% of phenols, most of which are capable of condensing with formaldehyde to form resins of the phenol-formaldehyde type (Novolak and Reson resins)[26,83]. Thus HL can serve as a source of aromatic phenolic substances and cheap biologically active compounds with a quinonoid structure.

In the course of the oxidative degradation of hydrolytic lignins, which is carried out in solution in ammonia at high temperatures (above 300 °C) in the presence of oxygen, the formation of low-molecular-weight acids is accompanied by the simultaneous oxidative ammonolysis reaction; it has been noted that it proceeds via a multiplicity of pathways owing

to the presence in the lignin macromolecule of a large number of functional groups having both the electron-accepting properties of the conjugation system and the electron-donating properties of the protons in the aromatic rings. The product of the oxidative ammonlysis of HL is ammonised lignin, which is characterised by a high content of strongly bound nitrogen not hydrolysable by acids, whose pyrolysis at temperatures up to 500 °C does not entail the formation of tars[84].

In oxidative ammonolysis, conjugated bonds accumulate in the lignin and, as a result of the incorporation of nitrogen in its macromolecule, its electrical conductivity rises sharply and its EPR signal intensifies, which indicates an appreciable delocalisation of the π electrons of the double bonds both within and between individual parts of the lignin macromolecule. As a consequence of the presence in HL of a system with conjugated bonds, it has the properties of an organic semiconductor, exhibiting paramagnetism, and its electrical conductivity is low[60,84,85].

One of the interesting features of the ammonised lignin as a product with the properties of an organic semiconductor is its catalytic activity in the decomposition of hydrogen peroxide. A distinct correlation has been noted between the catalytic activity of polymeric semiconductors having a conjugation system and their paramagnetic properties[84].

Ammonised lignin is biologically active. When it is introduced into soil in small amounts, the vegetative growth of the plant mass is found to be accelerated and the resistance to the action of decay-causing bacteria is enhanced.

Other applications of activated HL are also known, for example, in the preparation of its derivatives which are used as flotation agents instead of cyanides[86].

Hydrolytic lignin has also found applications in the manufacture of thermoplastics and reactoplastics[25,26,87-89].

A technology for the preparation of press-powders with heat and moisture resistances and improved dielectric parameters (compared with the press-powder from traditional resins of the 03-010-02 type), which can be used in the manufacture of electrotechnical articles instead of traditional resins, has been developed on the basis of the waste from the hydrolytic industry and agriculture[87].

Yet another promising application of HL in the plastics industry is the preparation from it of press-compositions for the manufacture of pressed articles at an elevated temperature with effective physicochemical parameters and reduced capacity for the absorption of water and susceptibility to wear. The optimum content of lignin is 10–15 wt.%, the sump and neutraliser sludge from the hydrolytic industry being used as a modifying agent, which greatly extends the material base for the manufacture of such articles and reduces their cost[89].

Since, in contrast to cellulose, stable colours can be imparted to HL by basic vat dyes, it has been suggested that lignin be dyed in order to modify its surface[25,88].

When insoluble dyes (Aniline Black, azo-dyes, etc.) are deposited on HL, its adsorption properties change significantly, so that the dyeing of lignin by appropriately selected dyes can be used in order to modify its surface properties. The dyed HL is of interest as an active filler for the poly(vinyl chloride) resin for the preparation of linoleum. The manufacture of such linoleum is very economical, because it makes it possible to reduce the consumption of the resin by 20–30% and the specific consumption of the plasticiser per m^2 of linoleum is reduced by 15–20%.[25] The dyed lignin can be employed as an active filler for thermoplastics, reactoplastics, and synthetic rubbers[88].

The considerable saving of thermoreactive resin is achieved by employing phenol-lignins or lignophenol-formaldehyde resins, obtained by the condensation of phenol and HL. Phenol-lignins are suitable for the manufacture of press-powders and their physicomechanical parameters are not inferior to those of the phenol-formaldehyde resin manufactured industrially[25].

One of the promising methods for the utilisation of lignin waste from the hydrolytic industry is its employment as thermally insulating materials; new methods of manufacture of constructional elements on their basis are being developed.

HL is used in the building industry, in the cement and brick industries (the preparation of lignoconcretes and other constructional materials based on lime, cement, and gypsum with added polymeric materials), in agriculture, and in other branches of the national economy[25,26,90], but the applications of lignin for these purposes are merely incidental and are not widely used on an industrial scale. Great potential possibilities for such employment of HL are inherent in the plastics industry, where the creation of filled polymeric materials using cheap active fillers constitutes an urgent problem[1].

V. SULPHITE LIGNIN (LIGNOSULPHONATES) AND ITS UTILISATION

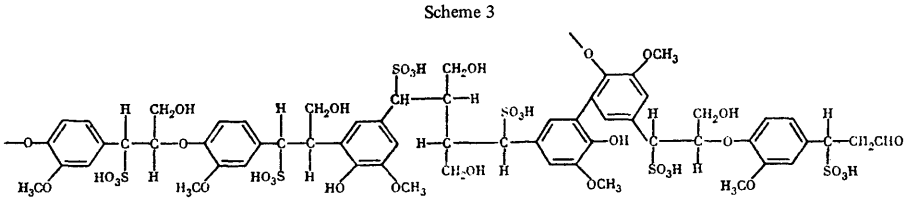
Lignosulphonates constitute the waste from the cellulose-paper industry in the manufacture of cellulose by the sulphite method. In this manufacturing cellulose-producing process, wood is heated with the digesting acid (an aqueous solution containing 2–10% of SO_2 in the form of free sulphurous acid and 1.3–2.5% of SO_2 as calcium bisulphite) with a stepwise increase of temperature to 145 °C. During the digestion, lignin is sulphonated. Almost the entire lignin and a large proportion of the carbohydrates accompanying cellulose can then be dissolved[25].

The chemistry of the sulphonation of lignin in sulphite digestions has still not been unambiguously elucidated but it has been shown that it may entail not only the sulphonation of lignin with formation of SO_3H groups but also the introduction of sulphate groups with formation of acid sulphate esters $R-OSO_3H$, in which the bond between sulphur and lignin is formed via oxygen[91].

The spent sulphite liquors contain aromatic substances whose composition is similar to that of lignosulphonic acids.

The lignosulphonic acids obtained in the manufacture of sulphite cellulose in the form of salts (calcium, sodium, ammonium, or magnesium lignosulphonates) have a variable composition, particularly as regards the content of carbonyl groups,

Scheme 3



depending on the degree of sulphonation and the methods of isolation. They are soluble in water, are titrated like strong inorganic acids, and are polyelectrolytes[92].

These acids constitute a polydisperse system with a wide range of molecular weights (2000–100 000).[30] The molecular structure of such an acid consists of a disordered, entangled, branched helix. The chemical structure of lignosulphonates has not been established, but by convention it can be represented in terms of the formula in Scheme 3.[25] During sulphite digestion, a major proportion of the lignin, in the form of lignosulphonic acids containing 4–6% of sulphur which form acid-containing groups of different strengths in the lignin[93], a large proportion of hemicelluloses, and other polysaccharides (including a certain amount of cellulose), tannins, and many inorganic subbstances pass into solution in the sulphite liquor[94].

The waste from the sulphite-cellulose industry consists mainly of the calcium salts of lignosulphonic acids and sugars [polysaccharides (pentoses) and monosaccharides (hexoses)] in proportions of approximately 2 : 1.[25] The reactions occurring in sulphite digestions have been examined in detail in the literature[23–25]. Valuable information about the structure of sulphite lignin is quoted by Forss and Fremer[42].

The hydrolytic and sulphonation reactions occurring in the acid treatment convert lignin into lignosulphonic acids with an extremely wide variety of molecular structures, including high-molecular-weight products with molecular weights in excess of 40 000. The content of such high-molecular-weight products is insignificant.

In order to isolate the lignosulphonates, the sulphite liquors are subjected to biochemical processing after separating cellulose, which results in the formation of a concentrate used for technical purposes.

Lignosulphonates are also manufactured in the form of liquid products and their amount manufactured in this form is ten times greater than in the solid state[94].

Free radicals, probably formed in the depolymerisation of lignosulphonates which constitutes a set of free-radical processes, have been detected in the lignosulphonic acids obtained from sulphite digestions[42,46,56]. However, the nature of these radicals could not be identified.

Thus the sulphite lignin in the form of lignosulphonates is the lowest-molecular-weight product among all the technical lignins and is characterised by a high solubility, also in water, and its principal practical applications are associated with this factor.

The varied applications of lignosulphonates substituted by univalent, bivalent, or polyvalent metals in various branches of industry and agriculture are based on their use as ion-exchange compounds, dispersants, surfactants, and fillers for natural tannides; their adhesive properties are also employed[25,26,94].

Lignosulphonic acids are of great interest as raw materials for the preparation of vanillin and vanillic acids[94].

Other applications of lignosulphonates are also known and these can be expanded by developing an extremely interesting method of biochemical processing of the organic materials in the liquor using not only carbohydrates but also lignin substances[86].

VI. SULPHATE ALKALI LIGNIN (KRAFT LIGNIN) AND ITS APPLICATIONS IN THE MODIFICATION OF POLYMERIC MATERIALS

Among all the types of industrial lignins, sulphate lignin, whose manufacture reaches an appreciable volume in view of the fact that three-quarters of the world production of cellulose (approximately 10 million tonnes annually) involves the sulphate method (the Kraft process), is most widely used in all industrial countries possessing wood as a raw material.

Alkali lignin is obtained as industrial waste in the manufacture of Kraft cellulose, where a mixture of sodium hydroxide and sodium sulphides is used as the base. The soda and sodium sulphate methods of preparation of cellulose are available. In these procedures wood is treated with a solution of alkali at 165°–175 °C.[48]

The principal difference between the soda and sodium sulphate methods of preparation of cellulose consists in the fact that the losses of part of the alkali, inevitable in the manufacturing process, are made good in the first instance by the addition of soda and in the second by the addition of sodium sulphate. The soda lignins are less soluble in organic solvents and are apparently more condensed than the sulphate lignins[95].

The spent dark solution obtained as a result of the digestion is called the black liquor and contains, together with inorganic substances, approximately half of the organic components of the initial wood, most of which is lignin. Since the technological cellulose digestion process by the sulphate method does not differ significantly from the soda method and the economic gain is fairly considerable, the sulphate method has almost completely displaced the soda method at the present time and henceforth we shall be dealing with sulphate alkali lignin or Kraft lignin.

The sulphate alkali lignin is sometimes called (not entirely correctly) "thiolignin", since a certain amount of organically bound sulphur (up to 2.5–3%) has been detected in it. However, this question remains controversial. It is most likely that the sulphur bound in organic compounds at the beginning of the sulphite digestion is split off during the subsequent digestion process and that the residual sulphur in the final product—the sulphate lignin—is most likely to be merely part of a side product stabilised as a result of side reactions[23,95].

In the sulphate method of manufacture of cellulose, virtually the only method of utilising the lignin obtained in the form of the black liquor remains its combustion. The part of the lignin contained in the "weak" liquor resulting from the washing of the cellulose and in the waste from the decomposition of the sulphate soap enters the waste water and pollutes it (waste water lignin).

In the Soviet Union and abroad rational ways of utilising sulphate lignin are being sought. The solution of this problem is at present urgently required also because in the industrial manufacture of cellulose an enormous amount of black liquors and waste water accumulate and their main organic component is lignin. In contrast to the other technical lignins isolated, Kraft lignins contain an increased amount of active acid groups (phenolic and hydroxyl), which largely determines their reactivity and the possibility of their practical employment for the reinforcement of rubbers and in the plastics industry. Sulphate lignins are therefore the most reactive and exhibit the highest chemical stability.

The difficulties in the employment of sulphate lignin are associated with the necessity to isolate it from the black liquors with a high yield of the lignin itself and this requires the development of a special technology[96,97].

For economic reasons, only two neutralising agents can be used to isolate lignin from the black liquor: H_2SO_4 and CO_2. When CO_2 is used, the yield of lignin is from 30% (carbonation without the application of pressure) to 70% (carbonation under pressure) of the amount present in the black liquor, while in the case where sulphuric acid is used, the amount isolated is in excess of 90%. A technology for the isolation of the carbon

dioxide and sulphuric acid sulphate lignins has been developed in the USSR. The chemical reactivities of these lignins hardly differ. However, the intrinsic cost of the carbon dioxide lignin (135 roubles per tonne) is 1.5 times higher than that of the sulphuric acid lignin[98,99].

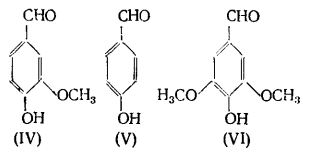
Pine, spruce, fir, larch, aspen, birch, popular and other types of wood as well as reeds, straw, and sawmill and wood processing waste are used as raw materials in the sulphate cellulose industry.

In the course of alkaline digestions and during the isolation of lignin from the black liquors, complex transformations associated with the rupture of hydrogen bonds under the influence of sulphide ions and alcoholic hydroxyls take place in the protolignin molecule, which greatly alters the structure of the Kraft lignin.

1. Characteristic Features of the Chemical Structure of Sulphate Lignin

Sarkanen, one of the senior foreign investigators of the chemistry of lignin, pointed out that the sulphate lignin precipitated from the black liquors on acidification is an ill-defined substance containing 2–4% of sulphur. However, its chemical structure is closest to that of natural lignin[72,100].

Bogomolov[48,96–98,101] and a number of foreign investigators[24†,55,102] have played a considerable role in the alkaline delignification of wood and the determination of the structure of sulphate lignin. The alkaline digestion of wood in the manufacture of cellulose constitutes a complex set of processes of different kinds, both chemical and physical. The chemical structure and properties of the resulting Kraft lignins are then significantly influenced by the conditions of the digestion and the origin of the wood employed (coniferous or deciduous)[24,25]. Lignins from gymnosperms (coniferous lignins) and lignins from angiosperms (deciduous lignins) differ in the products of their nitrobenzene oxidation: coniferous lignins give rise mainly to vanillin (IV) and small amounts of *p*-hydroxybenzaldehyde (V), while coniferous lignins produce vanillin and syringaldehyde (VI):



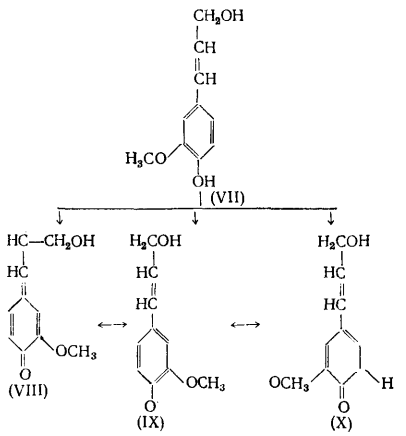
The chemical structure of the sulphate lignin isolated from the black liquors in the alkaline digestion has been examined and its various functional groups have been described in detail[24,102]. Reliable data have been obtained showing that the main bulk of the phenylcoumarin structures are converted during treatment into stilbene structures[30], which are formed when the radicals combine in accordance with Scheme 4 and apparently persist in the sulphate digestion and are present in Kraft lignin[28,30,102].

The stilbene structures cause the high reactivity of sulphate lignins and the reinforcement of polymers treated with such lignins.

† Chapter 12.

It has been established that Kraft lignin contains a considerable amount of phenolic hydroxyls, catechol groups, unsaturated quinonoid structures, aliphatic COOH groups, and other active structural elements containing double bonds.

Scheme 4



The principal distinctive feature of sulphate lignin is the presence of bound sulphur in amounts ranging from 1.5 to 3.0%, depending on the digestion conditions and the method of isolation of the lignin. A fragment of the structure of the sulphate lignin macromolecule is presented in Scheme 5:[28]

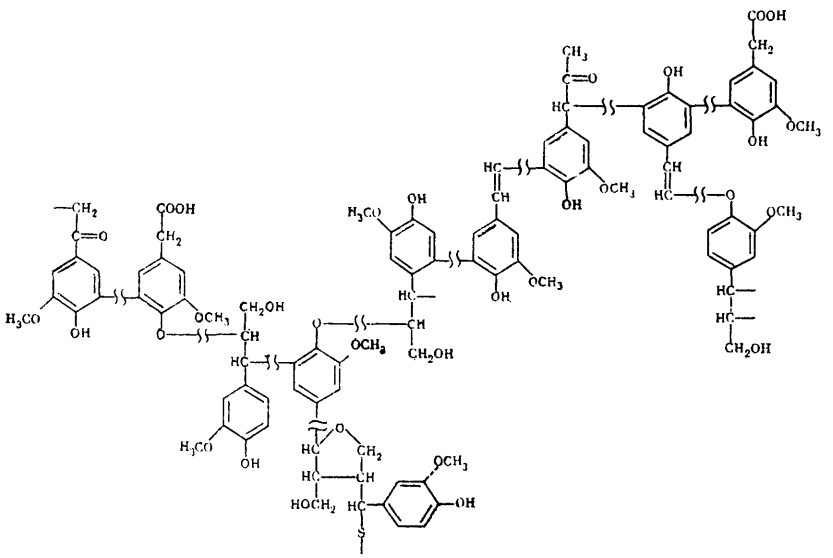
The alkaline digestion process constitutes a set of chemical reactions: the penetration of chemical reagents, the dissociation of lignin–carbohydrate linkages, thermal degradation of the lignin macromolecule, secondary reactions involving the condensation of fragments of this molecule, the removal of products from the reaction zone, etc. The reactions occurring in the alkaline digestion have been described in detail[24,30].

2. The Properties of Sulphate Lignin Responsible for Its Utilisation for the Reinforcement and Modification of Polymeric Materials

The EPR study of the paramagnetic properties of lignin provides great possibilities for the determination of the structures of native and technical lignins and also for the estimation of the modifying effect of Kraft lignin. As mentioned above, paramagnetic properties are characteristic of all kinds of technical lignins[42,56,60,85,94]. Free radicals were first detected in Kraft lignin by Kleinert and Marton[53] and these studies were continued in the cell of the EPR spectrometer in which wood was subjected to alkaline digestion[24,57,58]. It was established that the formation of the radicals R is the principal feature of the thermal wood delignification reactions and takes place when different methods are used for the delignification of wood at high temperatures (160° to 190 °C) regardless of the chemical nature of the raw material employed[24,54,56–58].

Free-radical reactions play a very important role in the alkaline delignification of wood particularly under the conditions of high speed digestions[54,55]. It has been noted that the concentration of the radicals R increases almost linearly with increase of the digestion time from 5 to 20 min (approximately in the first 0.5 h) and after the attainment of a

Scheme 5



maximum the concentration of R diminishes. This is probably a consequence of the fact that the alkaline delignification can involve two independent processes: degradation of the Kraft lignin macromolecules accompanied by an increase in the concentration of R and a decrease of the molecular weight and the subsequent condensation of the decomposition products accompanied by a decrease of the concentration of R and an increase of the molecular weight of the product.

However, when sulphate lignin is used for the modification of polymeric materials, it is necessary to know the character of the radicals R formed in it. Difficulties arise in the solution of this problem because it is impossible to resolve the hyperfine structure of the EPR spectra of the R formed. Many workers believe that natural lignins do not contain R at all and that the latter arise only on delignification of wood or in the course of its biological decomposition. The radicals R can also be formed as a result of the mechanodegradative processes during mechanical treatment with dissociation of covalent bonds[45,52,53,56,59].

This process has remained controversial hitherto, although recently it has been possible to obtain the EPR spectrum of Kraft lignin with a distinctive hyperfine structure at room temperature[45]. With increase of the digestion time, the spectrum changes: the signal loses its hyperfine structure and becomes of the singlet type. The EPR data for the soda and sodium sulphate treatments differ. Thus in the soda treatment the intensity of the EPR signal initially decreases and after a certain time (40 min) reaches a constant value, which permits the conclusion that two types of radicals are generated: unstable radicals whose concentration decreases with time from the start of the experiment and stable radicals whose concentration remains unchanged for 40 min.

In the sulphate treatment the hyperfine structure of the EPR spectrum was less distinct and disappeared faster than in the soda treatment. Furthermore, only a decrease of the EPR signal intensity was noted in the sulphate treatment.

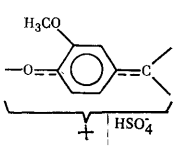
Comparison of data for the variation of the intensity of the EPR signal of lignin in the soda and sodium sulphate digestions shows that the influence of sulphur in the alkaline treatments can be explained by the inhibition of radical processes. When reducing agents (for example, sodium tetrahydroborate) are added to the liquors, the concentration of R falls and the hyperfine structure decreases much faster than in the soda digestion. The primary electronic excitation centre in the lignocarbohydrate complex is a semiquinonoid radical formed, which is fairly stable for some time[45].

The reactions of the radicals formed in the alkaline digestion cause the cross-linking of lignin and the increase of its molecular weight during the initial periods of the digestions. Inhibition may be achieved by introducing reducing agents ($NaBH_4$, Na_2S, cysteine, hydrazine, and thioglycolic acid). whose reduction potential is higher than that of lignin and carbohydrates in an alkaline medium, and by recombination reactions between lignin radicals and a specially introduced substance[103].

There exist two points of view concerning the nature of the increase of the molecular weight of lignin in alkaline digestions: the first explains the increase of the molecular weight by polycondensation processes and the second—by the interaction of the radicals. Both concepts remain controversial.

In addition to the view which explains the paramagnetic properties of lignin by the formation of the radicals R, it has been suggested that the paramagnetism of lignin has a radical nature[104] which for technical lignins is attributed to the presence of paramagnetic carbonium centres in their molecules.

Stable carbonium centres are formed in all technical lignins, and their stability can be explained both by steric factors and by their ability to combine with anions in solution to form carbonium salts:



The proposed mechanism of the formation of carbonium centres makes it possible to discover the cause of the differences between the sodium sulphate and soda digestions and also to explain the sharp increase of the EPR signal intensity of alkaline preparations of lignin in protic solvents, for example, in concentrated sulphuric acid. The stability of the paramagnetic carbonium ions may be influenced favourably also by other nucleophilic additives, such as amines, mercaptans, etc.

Taking into account the latter data, one may assume that the real nature of the paramagnetism of lignin is of a dual kind.

Interesting results have been obtained on irradiation of lignin and its model compounds with ultraviolet light at a wavelength of 300–400 nm directly in the EPR spectrometer[68]. The resulting spectra permitted the conclusion that phenoxy-radicals are formed preferentially.

The formation of phenolic compounds in the thermal decomposition of lignins, including alkali lignin, has also been discovered[70,73].

The inhibiting role of lignin (as a result of the formation of quinone methide structures) is indicated by the data of Zoldners et al.[105] The results reveal yet another promising application of lignin as an inhibitor and stabiliser with respect to the action of light for polymeric materials and compositions based on them (particularly compositions based on polypropylene), since there is a correlation between the stability of organic free radicals and the efficiency of their reaction[106].

Sulphate lignin is a lamellar amorphous polymer with a polydisperse structure which tends to undergo association and is characterised by a definite molecular order in its structure[107,108].

The molecular weights of Kraft lignins were first determined by Marton, Marton, and Lindberg[102,109,110] by different procedures and in different solvents and showed a fairly wide scatter: the weight-average molecular weight $\overline{M}_w$ was in the range 5600–25 000 and the number-average molecular weight $\overline{M}_n$ was in the range 1000–20 000. The ratio $\overline{M}_w/\overline{M}_n$ was 2.2 for the sulphate lignin from conifers (pine lignin) and 2.8 for the sulphate lignin from deciduous trees, which may indicate an appreciable dispersity.

The study of the molecular weight and the molecular weight distribution (MWD) of sulphate lignins showed that $\overline{M}_w$ of lignin is determined both by the digestion temperature and the sulphide content of the digestion liquor[96,111,112]. The values of $\overline{M}_w$ obtained for sulphate lignin varied from 4000 to 24 000 for digestions according to isotypical plots and from 7000 to 31 000 for stepwise digestions. The soda lignins isolated from the mass of cellulose in the soda digestion had a higher value of $\overline{M}_w$ than sulphate lignins.

The wide range of variation of the $\overline{M}_w$ of sulphate lignins cannot be attributed solely to the method of measurement of their molecular weight. It is probably caused by the different degrees of degradation of the soluble lignin in the digestion process or, possibly, by the association of the alkali lignin in solution, which was not taken into account in the early investigations[30].

Like lignosulphonates, sulphate lignins with a low molecular weight exhibit a high dispersing power, which is determined from the decrease of the viscosity of an aqueous suspension of rutile (titanium dioxide) on dissolution of a specific amount of lignin. The high dispersing power of Kraft lignin led to its employment in the form of industrial colloids (dispersants, binders, fillers, and gel-forming agents)[24] (Chapter 13).

A sulphate lignin paste for the building materials industry and powdered sulphate lignin for the technical rubber article industry are manufactured in the Soviet Union. The study of the properties of sulphate lignins produced by industry showed that they consist of products with a fairly high molecular weight of 4500–7500 and a degrees of polydispersity of 3.3–3.9.[97]

Technical lignin is a brown powder with a particle size from 100 to 200 μm, the 100–125 μm particles constituting the largest fraction. Particles of this size are largely spherical in a slightly fused envelope, while the larger particles consist of aggregates of the spherical particles. When sulphate lignin is dried (in the upper drying chamber) and also when it is vibromilled, not only its aggregates but also the spherical particles themselves are disrupted.

The vibromilled lignin particles have a high specific surface (up to 23 $m^2\ g^{-1}$) and are characterised by an excess of free energy, which may be the cause of their adhesion to one another and the formation of a complex of secondary particles whose size approaches to the optimum particle size of the non-comminuted lignin. The density of Kraft lignin is approximately 1300 kg m^{-3}.[22]

When the optimal technological parameters are maintained in the manufacture of sulphate lignin, the finished product has a fairly constant functional composition in terms of the ash, acid, and sulphur contents as well as the contents of water-soluble and tarry substances.

The infrared spectra of industrial batches of sulphate lignin are fairly isotypical both as regards the presence of absorption bands at the same wavelengths and the relative optical densities.

The thermal properties of lignin were already noted above. The presence of lignin in wood is the cause of its thermal softening, which begins in the temperature range 120° to 160 °C. The softening temperature (glass point) of lignin varies appreciably depending on its source and method of isolation[24] (Chapter 13). Sulphate lignins sinter at approximately 200 °C and tend to pass to a fluid state at elevated temperatures.

Important properties of sulphate lignin include its capacity for adhesion, which is a function of temperature, and its sorption properties[24,113].

On treatment with water, the degree of sorption of moisture increases, moisture acting as a low-molecular-weight diluent which reduces the transition temperature (T_g).

The solubility of lignin in various solvents depends on its sorption properties. It has been established that the action of solvents on lignin is a function of the cohesion energy density and the ability of the solvent to form hydrogen bonds. The maximum solvent power in terms of the Hildebrand parameter δ, defined as the square root of the cohesion energy density, is then observed for $\delta = 11\ cal^{1/2}\ cm^{-3/2}$. The solvent power of solvents with δ between 10 and 11 in relation to lignin increases with increasing ability of the solvent to form hydrogen bonds.

The study of solubility data has shown that the behaviour of lignin with respect to solvents and other macromolecules cannot be explained solely on the basis of the parameter characterising the ability to form hydrogen bonds, whose measure is the shift $\Delta\lambda$ of the infrared absorption of the OD group when the solvent is mixed with CH_3OD. However, water, which is usually a "poor" solvent for lignin, has the very high parameter $\delta = 23.4\ cal^{1/2}\ cm^{-3/2}$. On this basis one may conclude that, in estimating the solubility, one must take into account the overall effect of the polarity of the solvent molecules[110].

It has been shown that the fractions of lignin with a smaller molecular weight are soluble in solvents with a wider range of δ and $\Delta\lambda$ than the fractions with higher molecular weights. "Good" solvents for lignins must have $\delta \cong 11$ and $\Delta\lambda \geq 0.14$.[114]

From this standpoint, "good" solvents for sulphated lignin are dimethyl sulphoxide, dimethyl formamide, acetone, dioxane, pyridine, ethanol, methylcellosolve, and certain others, while "moderate" solvents are ethyl acetate and others[110].

Evidently the infrared spectra and solubility parameters of lignin provide information about its molecular size, the nature of its intermolecular interaction, and the general properties of the product. This applies particularly to the interaction with a single solvent. When mixed solvents are used, the problem is greatly complicated, but, with the aid of the two-parameter theory, it is possible to predict roughly the relation between the structure and solubility of lignins in binary and even ternary systems in terms of the reaction parameter (the Flory parameter).

3. Other Types of Sulphate Lignins

(a) *The ligno-tail product of the sulphate-cellulose industry.* In the alkaline delignification of wood, not only lignin but also resin and aliphatic acids, neutral substances, phenols, a proportion of carbohydrates, and other substances of organic and inorganic origin forming part of wood pass into the digestion solution called the "black liquor"[48]. When the black liquor is allowed to stand, the resin and aliphatic acids in the form of sodium salts coagulate and rise to the surface entraining the accompanying substances. The coagulation product is called the sulphate soap which has a complex composition, containing lignin and lignin-like substances among others.

The sulphate soap is in its turn decomposed with sulphuric acid, after which the reaction mixture is divided into three-layers: the tall oil brick, crust, and solid salts. The reaction mixture prior to separation into three layers is called the ligno-tall product and is a valuable raw material for the regulation of polymeric materials. The ligno-tall product (a mixture of tall oil and crust—lignin and lignin-like substances) contains up to 60% of tall oil, which is a mixture of aliphatic and resin acids, an insignificant amount of non-hydrolysable products, and approximately 40% of lignin.

The ligno-tall product (LT) can be obtained by mixing the markedly dustlike sulphate lignin powder with tall oil in proportions of 2 : 1.

The waste from the sulphate-cellulose industry can also be used to obtain the LT product: the acid water from the sulphate soap decomposition apparatus, light oil, pitch, etc.[97] A distinctive feature of the LT substances obtained in this way is a high ash content, which necessitates the removal of inorganic substances from them.

The LT substances can be mixed with a suspension of sulphate lignin in proportions of 1 : 2 and the new suspension of tall oil and lignin then yields a crude ligno-tall product which has approximately the same characteristics as dry powdered sulphate lignin. The applications of these lignins in the polymeric industry are approximately the same.

(b) *Lignin obtained from waste water (sludge lignin) from the sulphate-cellulose industry.* When the waste water from the sulphate-cellulose industry is purified, a large number of wash waste is produced—a sludge, which consists of waste water lignin and is a valuable chemical raw material. The sludge lignin provides a virtually inexhaustible source of raw material, since it accumulates in enormous amounts in waste dumps after the waste water has passed through the biological and chemical purification stages[99,115].

Industrial waste water from the sulphate-cellulose manufacturing process contain a large amount of lignin and organic substances. The purification of such water and the processes whereby they are rendered safe are achieved by a biological or chemical method and in many instances, when extensive purification is required, a combined method of purification is used.

The biochemical purification consists in the reduction of the biological and chemical consumption of oxygen as a result of the oxidative action of the "active silt" and the adjustment of the oxygen content to the norms established by sanitary requirements for industrial water released into water reservoirs. However, after such purification a considerable amount of dissolved organic substances remains in the water.

In the subsequent chemical purification of waste water by treatment with flocculants (aluminium sulphate and polyacrylamide) coagulation takes place and the colloidally dispersed particles, which are not decomposed in the biological purification, are removed. The water untreated with the active silt can be purified chemically with alumina and polyacrylamide[99,115].

The sludge lignin isolated has a dark-brown colour, contains up to 98% of moisture which is difficult to remove, and gives rise to stable lumps on drying, which are difficult to grind. The sludge lignin must be dried and the drying process can be carried out twice.

The main part of the precipitate extracted from waste water is a modified sulphate lignin, since, after prolonged treatment with active silt, it undergoes a whole series of processes which alter somewhat its structure[116].

Sludge lignin has a high ash and active silt content. In its activity, the waste water lignin is not inferior to Kraft lignin and can find extensive applications for the reinforcement of rubbers in the technical rubber industry and for the modification of polymers in the plastics industry.

4. The Employment of Sulphate Lignins for the Modification of Polymeric Materials

The applications of sulphate lignins can be divided into three groups: (1) combustion; (2) the use of the surface-active properties of the water-soluble lignin salts; (3) condensation of lignin[24].

In all the industrially developed countries sulphate lignin is used mainly as a fuel in regeneration furnace systems. This application cannot be regarded as normal, because lignin is a valuable chemical raw material and its employment for the generation of power is an example of an uneconomic utilisation of a valuable natural polymer such as sulphate alkali lignin.

Problems concerning the employment of sulphate lignin for the stabilisation of emulsions, in the processing of cement and ceramics, in the dispersion of dyes, pigments, etc., where the surface-active properties of the water-soluble lignin salts are used, and in the preparation of thermoreactive resins in combination with phenols, urea, and other products, have been fairly thoroughly described in the literature. Sulphate lignin can be used to prepare valuable low-molecular-weight products: dimethyl sulphide (the starting material for the manufacture of dimethyl sulphoxide, which is a very valuable solvent), phenolic derivatives more valuable than those obtained from petroleum, vanillin, etc. The possibility, in principle, of using sulphate alkali lignin in the form of liquid self-hardening mixtures in the casting industry, etc. has been demonstrated recently[23-25,48,96,117,118].

Among all the technical lignins, sulphate lignins are chemically the most reactive and have therefore been used for a long time to modify polymers. The majority of investigators believe that chemical bonds may be formed between the lignin macromolcule and the macromolecules of synthetic polymers, although the question of the nature of these bonds

remains open. The oldest and the most familiar application of lignin as a component of polymeric materials involves the reinforcement of raw rubbers. Very extensive studies, published both abraod and in the USSR, have been devoted to this problem[9,15,16,96,119–125].

A distinctive feature of the preparation of lignin-filled rubbers is that, in order to reinforce the latter, lignin is introduced at the latex stage, since the introduction of powdered lignin into dry rubber does not lead to the "reinforcement" effect. It is believed that the reason for this is the binding of lignin particles to one another by hydrogen bonds, which leads to condensation and growth of its particles and prevents the dispersion of the lignin particles during the rolling of rubber[9,119].

The introduction of lignin into rubber at the latex stage greatly complicates and increases the cost of the technology of its manufacture, since the usual method for the preparation of the parent lignin–rubber mixture consists in the dissolution of lignin in an aqueous solution of alkali, mixing of the alkaline solution with the rubber latex, heating the mixture, and the joint coagulation of the rubber and lignin by pouring the mixture into a solution of acid while stirring. The reinforcing effect of lignin is determined by its particle size, which depends on the precipitation conditions and certain other factors[9]. In the parent mixture the lignin is not bound to rubber by chemical bonds. The reinforcing effect of lignin increases appreciably when lignin is precipitated in the presence of sodium silicate[16].

The mechanism of the reinforcement of raw rubbers by sulphate lignin can be accounted for mainly by its surface-active properties and the coagulate is therefore precipitated in the form of fine particles. This leads to the formation of a material with low stress parameters for 300% elongation and a high hardness, so that the lignin-filled vulcanisates exhibit a lower resistance to wear than carbon-black filled rubbers.

In order to eliminate the above defects, the lignin-rubber mixture is treated with polyisocyanates and is used in the manufacture of rubbers for car tyres. The polyisocyanates employed are di- and tri-isocyanates of different chemical structure in amounts ranging from 1 to 10 parts per 100 parts of rubber (dry weight)[126]. The articles obtained from such a composition have improved operating characteristics, in particular the stress corresponding to 300% elongation and the resistance to abrasion increase by a factor of 1.5–2.0 (depending on the content of the additive).

The mechanism of the reinforcement of rubbers by lignin is fairly complex and has not been completely investigated. Apart from the physical explanation, associated with the surface-active properties of lignin, there is a chemical explanation of this phenomenon. The reinforcement of rubbers by alkali lignin can be accounted for by the interaction of the active groups of lignin with the double bonds or active groups of the rubbers—the formation of hydrogen bonds between the hydroxy-groups of lignin and the π electrons of the double bonds of the rubbers[119]. When isocyanates are introduced, the high reactivity of the isocyanate groups promotes the rupture of the hydrogen bonds, which are unable to reinforce the dry lignin and the latter is thus converted into an active series.

Sludge lignin can be used successfully as an active filler and reinforcing agent for polymeric materials[127].

Lignin-filled rubbers can be obtained in two ways: (1) the coprecipitation of lignin and rubber from a lignin–latex mixture by the method indicated above and (2) by introducing hydrated lignin into rubber with the aid of rubber mixing equipment. Both these procedures are technologically complex and uneconomical and have not therefore found extensive industrial applications.

The vulcanisates filled with dry lignin are characterised by a tensile stress σ_t not exceeding 6.0 mN m^{-2}.

Lignin–oil pastes can be used as lignin products isolated from black liquors for the reinforcement of raw and cured rubbers. They are obtained by mixing hydrated lignin, containing approximately 60% of moisture, with a plasticiser (tall oil, pine resin, PN-6 oil), after which moisture is evaporated from the resulting mixture with continuous stirring (the stirring temperature is 60–70 °C). Simultaneously with drying, the lignin is dispersed in the plasticiser, which prevents the agglomeration of the lignin particles and tends to increase the degree of their dispersion. Outwardly, the lignin–oil paste consists of a powder or solid lumps of dark-brown colour, depending on the type of plasticiser. Such a paste can be introduced into rubbers using the normal rubber mixing equipment[123].

Yet another method for the isolation of lignin from black liquors involves its precipitation in the presence of water-soluble additives (low-molecular-weight alcohols, aldehydes, ketones, or emulsifiers) which promote the formation of a highly disperse product. The vulcanisates obtained using these lignins have high values of the tensile stress: $\sigma_t = 16$ and 18 mN m^{-2} respectively.

Dry sulphate lignin is of considerable interest for the filling and modification of thermoplastics in order to obtain frost-resistant polypropylene (PR) compositions and also in the reprocessing of waste from polymeric materials. Studies have been carried out on the creation of composite materials using sulphate alkali lignin based on polyolefins (PO)—materials of the type of poprolin, including preparations based on secondary polyethylene obtained from used articles[17–21,61–67,128–138].

The study of the character of the interaction of the ingredients of the polymer composition under processing conditions is very important for the specific modification of the basic polymer by sulphate lignin (when the content of the latter is up to five parts) and for the determination of the technological regime for the conversion of poprolin materials into articles.

The EPR method is of practical importance for such purposes. It has been established by this method that paramagnetic polypropylene and lignin centres formed at the processing temperatures interact at the interface between the two phases (polypropylene–lignin); it has been shown that the interaction has a radical mechanism[19,64,66,97]. The results agree with data obtained in the study of free radicals in the formation of the carbon black–raw rubber gel. It has been observed that during the rolling of the rubber in the course of its processing, free radicals are formed and interact with the polymer via a radical mechanism[140,141]. An interesting feature of this process is the approximately linear relation between the ratio of the EPR line widths in air and *in vacuo* ($\Delta H_{air}/\Delta H_{vac}$) and the specific surface of the carbon black, which indicates the surface character of the interaction of some of the spins, capable of participating not only in the formation of the carbon black–raw rubber gel but also in the agglomeration of the carbon black particles.

By analogy with data obtained in the study of carbon black by EPR, the concept of c_a/c_0—the relative concentration of the active free radicals on the surfaces of the lignin particles—was introduced for the interpreation of the results in the polypropylene–lignin system and the differentiation of the free radicals present on the surfaces of the lignin particles and responsible for the interaction with the polypropylene; according to the literature[19,129,132], the relative concentration represents the different $c/c_{0\,NaCl} - c/c_{0\,PP}$, where c is the overall concentration of the lignin free radicals at the experimental temperature, c_0 the concentration at room

temperature calculated with a correction for the Curie law, c_0 NaCl the concentration of the radicals R of lignin in the inert NaCl diluent, and c_0 PP the corresponding concentration in the polypropylene matrix. This approach makes it possible to follow the kinetics of the interaction of the paramagnetic centres of lignin and the radicals R of polypropylene at the processing temperatures, to assess its character and to optimise the polymer composition and the optimum lignin content.

In order to improve the operating characteristic of poprolin (to reduce the embrittlement temperature T_{br} and increase the frost resistance), a low-molecular-weight plasticiser dioctyl sebacate (DOS) was introduced into the polypropylene–lignin system, which resulted in the formation of a frost-resistant material—poprolin-1.

It follows from the EPR data that the introduction of DOS into poprolin disrupts the interaction between the paramagnetic centres of lignin and polypropylene, which entails a decrease of c_a/c_0. The attempts to intensify the disrupted interaction by introducing an additional amount of lignin (in excess of the optimum value for the given composition) did not lead to the desired results. Tests showed that the disrupted interaction cannot be restored by introducing fillers of the type of titanium dioxide, which has been stated[24] to be capable of adsorbing lignin, wetting its surface and leading to a more effective dispersion of the plasticiser and lignin in the polymer matrix. Furthermore, the introduction of titanium dioxide prevents the interaction of lignin with DOS, stimulating the interaction of lignin with polypropylene and leading to an enhanced stability of the system[64,65]. These data indicate the possibility of regulating by the above procedures the properties of complex materials important for practical applications.

The study of the rheological characteristics of poprolin-1 showed that the introduction of the optimum amount of lignin (three parts) reduces its fluidity, which entails the transition of the flow curve to the region of the lowest shear stresses compared with the initial polypropylene[19,61,128,139]. This greatly facilitates the processing of poprolin-1, the articles obtained from it being characterised by effective operating characteristics under the conditions of low temperatures (compared with the basic polypropylene) and the range of their utilisation is greatly increased.

One of the procedures in the technology of the processing of plastics designed to increase the quality of the polymeric materials and to increase the useful lifetime of the articles obtained from them is known to involve the introduction of antioxidants in order to suppress oxidation processes occurring under the influence of various factors (high temperatures, solar radiation, etc.). Phenols, as inhibitors absorbing in the ultraviolet, have come to be widely used among antioxidants[142]. The photoreaction of phenols leads to the formation of phenoxy-radicals, which in their turn undergo a photoreaction in the polymer matrix and their subsequent fate depends on their reactivity, temperature, concentration, and the type of polymer matrix[142–144].

In terms of their chemical structure, lignins can be assigned to the class of sterically hindered phenols. On the other hand, the involvement of sterically hindered phenols in radical reactions reduces to the initial abstraction of the hydrogen atom from the hydroxy-group of the phenols with formation of a phenoxy-radical, i.e. the behaviour of the sterically hindered phenol in radical reactions is determined by the properties of the phenoxy-radicals formed. It is known that the O–H bond energy in sterically hindered phenols is somewhat lower than in unsubstituted phenols, which facilitates, on the one hand, the homolytic dissociation of the given bond with formation of phenoxy-radicals, and on the other hand, leads to the formation of thermodynamically more stable species—stable free radicals[144]. The stability of the radicals R formed in the reaction of the antioxidant has a significant influence on the kinetics of the ageing of the polymeric materials, since the probability of the involvement of these radicals, following the enhancement of their stability, in recombination reactions in subsequent processes diminishes, which promotes an increase of the inhibiting effect of the antioxidant. The character of such stability is to a large extent determined both by structure factors (intramolecular stabilisation) and by the interaction of the radicals with the medium (intermolecular stabilisation). The experimental results, showing that lignin or its degradation products can be used as thermostabilisers for polypropylene at its processing temperatures (in excess of 200 °C) and as inhibitors in its photoageing process, may serve as confirmation of the above considerations[64,132,145,146].

However, data have been obtained recently showing that sulphate lignin can be used as a photomodifying additive to polypropylene and that it does not affect its degradation on prolonged irradiation. At the same time it can greatly reduce the efficiency of light stabilisers operating in accordance with an inhibition mechanism, so that, in order to improve the light stability of lignin-containing compositions, it is desirable to introduce additional substances belonging to the class of u.v. absorbers or dyes. Since the ligno-tall product contains simultaneously structure-forming (lignin), reinforcing (aliphatic acid salts), and plasticising (tall oil) substances, it is a complex modifying agent[139].

The application of the ligno-tall substances greatly simplifies the technology of the preparation of frost-resistant polypropylene of the type of poprolin-1 because the necessity for the initial introduction of the scarce and expensive DOS is eliminated.

The application of sulphate alkali lignin in the preparation of compositions based on polyolefins using secondary low-density polyethylene (SLDPE), obtained from worn agricultural sheeting, is of great theoretical and practical interest[20,21,134–136].

A factor promoting the formation of such composite material (poprolin-2) was the fact that SLDPE is a product activated during use as a consequence of photo-oxidative reactions in the LDPE during the use of the sheeting. The kinetics of the oxidation of the LDPE depend to a large extent on the degree of branching of the polymer and the oxidation proceeds via the formation of polymeric hydroperoxides (POOH) and ketones with the possible occurrence of radical reactions in the photodecomposition of ketones via a Norrish type I mechanism[147,148]. At the same time an additional amount of radicals R are formed in the SLDPE, their concentration being somewhat greater than in LDPE and lower than in polypropylene[19]. As a result of the formation of an additional amount of free radicals in the secondary polyethylene matrix, the effect of the interaction of the polymeric components in poprolin-2 (SLDPE and polypropylene) with lignin is much stronger, which increases the stability of the composition as a result of the improvement of the operating stability of the system.

Materials of the type of poprolin have been successfully converted into articles of extrusion (film materials, including coextrusion films based on moderate-pressure polyethylene, tubes, and sheets), by casting under pressure (transport packing capable of repeated use for branches of industry manufacturing food products), and by mechanothermomoulding and rotation moulding (large packing for various branches of the national economy)[131,133,137].

A distinctive feature of articles made of poprolin materials is their effective physicomechanical and operating characteristics (compared with various polyethylenes and even polypropylene) and the lower intrinsic cost of the articles obtained from them. The poprolin materials are more susceptible to technological procedures and have a better capacity for being worked compared with the basic polymer. The use of poprolin provides the national economy with a significant economic gain by increasing the useful lifetime of articles in the course of their employment, and promotes the rational employment of natural resources, protection of the environment, and the expansion of the reserves of a scarce primary polymeric raw material as a result of the employment of a secondary raw material.

The study of the behaviour of lignin in the modification of wood by synthetic polymers is of interest because it is one of the high-molecular-components of wood. The possibility of radiation grafting onto isolated lignin of various synthetic polymers, for example styrene, methyl methacrylate, and acrylonitrile has been demonstrated[149–154]. It has been established that the radiation-chemical modification of wood with styrene involves the cross-linking of lignin and polystyrene, in which stable free radicals play an appreciable role[155].

Studies of the polymerisation of styrene with hydrochloric acid lignin and Kraft lignin with chemical and radiation initiation have been carried out by non-Soviet workers[150,155,156], who, with the aid of model lignin compounds (guaiacol, 2,6-dimethoxyphenol, and isoeugenol), discovered its inhibiting effect on the polymer. The graft copolymerisation of lignin and styrene takes place as a result of the transfer of the chain of the growing polymer radicals to the lignin units containing phenolic groups, which have an inhibiting effect on the kinetics of the process, resulting in its retardation, which entails the formation of a graft copolymer with a reduced molecular weight.

Sulphate lignin has an analogous effect on the thermal initiation of styrene in dimethyl sulphoxide in the presence of chemical initiators[157]. A considerable increase of the inhibiting effect of lignin in the presence of oxidants (for example, atmospheric oxygen), owing to the formation of quinonoid structures for both chemical and radiation methods of initiation has been noted.

The graft copolymerisation of various monomers with wood lignin leads to a new way of creating mixed composites with a graft structure as a result of the mixed chemical combination of natural and synthetic polymers possessing a valuable set of properties.

According to structural ideas, grafting can occur on the surface of the polymer particle (surface grafting) and within it (block grafting), which depends on the process conditions. By creating conditions for grafting via one procedure or another, it is possible to regulate within wide limits the properties of the resulting composite materials[158].

Like hydrolytic lignin, sulphate lignin can be used for condensation with phenols in order to obtain lignophenol-formaldehyde resins. In the polycondensation reaction the phenol adds to lignin via a ring hydrogen atom but not a hydroxyl hydrogen atom, which follows from the solubility of phenol-lignin in alkali. The introduction of a third component (formaldehyde) makes it possible to obtain fusible and alcohol-soluble resins whose properties are analogous to those of industrial products[25].

Latvian investigators suggested that hydroxypropylated lignins (HPL) be obtained on the basis of modified lignoorganosilicon oligoethers and epoxypropane[159], which constitutes an extremely promising application of technical lignins. A method for the preparation of polyurethane foam materials (on the basis of HPL) has been developed; HPL can be used as fillers (based on technical lignins) for plastics.

There exist data concerning the utilisation of modified sulphate and sulphite lignins for the preparation of a composite friction material with up to 15 wt.% of lignin[160].

A new and promising application of all types of technical lignins in the light of the fulfilment of resolutions concerning the rational employment of natural resources and the protection of the environment involves the development of highly filled polymeric materials based on lignin—lignoplastics. This task is extremely complex and laborious, since it requires very extensive scientific and technological investigations and also the creation of industrial comminuting equipment. However, a realistic basis for its successful fulfilment already exists.

REFERENCES

1. B.A.Rozenberg and N.S.Enikolopyan, Zhur.Vses. Khim.Obshch.im.Mendeleeva, 1980, **25**(5), 524.
2. D.V.Ivanyukov and M.L.Fridman, "Polipropilen: Svoistva i Primenenie" (Polypropylene: Properties and Applications), Izd.Khimiya, Moscow, 1974, 272 pp.
3. Yu.G.Kuz'mina, "Proizvodstvo i Primenenie Kompozitsii s Napolnitelyami na Osnove Sopolimerov Stirola i Poliolefinov. Obzornaya Informatsiya. Ser.Polimerizatsionnye Plastmassy" (The Manufacture and Applications of Filled Compositions based on Styrene–Polyolefin Copolymers. Review Information. Polymerisation Plastics Series), Izd.NIITEKhIM, Moscow, 1977, 43 pp.
4. G.Forger, Plast.World., 1980, **38**, 60.
5. "Fillers for Polymeric Composite Materials" (Translated into Russian from English), Izd.Khimiya, Moscow, 1981, 736 pp.
6. "Modifikatsiya Napolnitelei dlya Termoplastov. Obzornaya Informatsiya. Ser Polimerizatsionnye Plastmassy" (Modification of Fillers for Thermoplastics. Review Information. Polymerisation Plastics Series), Izd.NIITEKhIM, Moscow, 1977, 82 pp.
7. G.M.Barsegyan, Abstracts of Candidate's Thesis in Technical Sciences, Mendeleev Moscow Institute of Chemical Engineering, Moscow, 1970, 27 pp.
8. E.P.Nikulina, "Khimicheskaya Promyshlennost' za Rubezhom" (The Chemiccal Industry Abroad), Izd. NIITEKhIM, Moscow, 1978, No.5, p.41.
9. G.Kraus (Editor), "Reinforcement of Elastomers" (Translated into Russian), Izd.Khimiya, Moscow, 1968, 484 pp.
10. E.G.Lyubeshkina, M.S.Kurilo, M.S.Akutin, et al., "Tezisy Dokladov Simpoziuma 'Sintez, Modifikatsiya i Pererabotka Poliolefinov'" (Abstracts of Reports at the Symposium on 'The Synthesis, Modification, and Processing of Polyolefins'), Baku, 1967, p.52.
11. E.G.Lyubeshkina, L.T.Belova, and V.E.Gul', "Tezisy Dokladov VI Vsesoyuznoi Konferentsii po Khimii i Ispol'zovaniyu Lignina" (Abstracts of Reports at the VIth All-Union Conference on the Chemistry and Utilisation of Lignin), Izd.Zinatne, Riga, 1976, p.146.
12. V.L.Klimenko, V.N.Nepomnyashchii, and R.E.Tsipman, Plast.Massy, 1974(12), 12.
13. Yu.V.Pokonova, V.A.Proskuryakov, and V.I.Levanovski, "Khimiya i Tekhnologiya Slantsevykh Fenolov" (The Chemistry and Technology of Shale Phenols), Izd.Leningrad.Gos.Univ., Leningrad, 1979, 191 pp.
14. K.A.Pechkovskaya "Sazha kak Usilitel' Kauchuka" (Carbon Black as a Reinforcing Agent for Raw Rubber), Izd.Khimiya, Moscow, 1968, 215 pp.

15. J.Keilen and A.Pollak, Ind.Eng.Chem., 1947, **39**, 480.
16. J.Gatto, Rubber World, 1972, **165**(5), 127.
17. V.E.Gul' and E.G.Lyubeshkina, Dokl.Akad.Nauk SSSR, 1965, **165**, 110.
18. V.E.Gul' and E.G.Lyubeshkina, Plast.Massy, 1966(1), 68.
19. E.G.Lyubeshkina, L.T.Belova, M.L.Fridman, et al., Mekh.Polimerov, 1977(3), 535.
20. USSR P.771 126, 1978; Byul.Izobret., 1980(38), 144.
21. E.G.Lyubeshkina, M.L.Fridman, V.I.Berezkin, and V.E.Gul', Plast.Massy, 1982(1), 19.
22. B.D.Bogomolov, "Khimiya Drevesiny i Osnovy Khimii Vysokomolekulyarnykh Soedinenii" (The Chemistry of Wood and the Principles of the Chemistry of High-molecular-weight Compounds), Izd.Lesnaya Promyshlennost', Moscow, 1973, 400 pp.
23. N.N.Shorygina, V.M.Reznikov, and V.V.Elkin, "Reaktsionnaya Sposobnost' Lignina" (The Reactivity of Lignin), Izd.Nauka, Moscow, 1976, 368 pp.
24. K.V.Sarkanen and C.H.Ludwig (Editors), "Lignins" (Translated into Russian from English), Izd.Lesnaya Promyshlennost', Moscow, 1975, 732 pp.
25. M.I.Chudakov, "Promyshlennoe Ispol'zovanie Lignina" (Industrial Utilisation of Lignin), Goslesbumizdat, Moscow, 1962, 183 pp.
26. M.I.Chudakov, Symposium, "Khimiya Drevesiny" (The Chemistry of Wood), Izd.Zinatne, Riga, 1968, Vol.1, p.311.
27. K.Freudenberg, Holzforschung, 1964, **18**, 3.
28. N.N.Shorygina, Symposium, "Khimiya Drevesiny" (The Chemistry of Wood), Izd.Zinatne, Riga, 1968, Vol.1, p.7.
29. S.M.Manskaya, Symposium, "Khimiya i Ispol'zovanie Lignina" (The Chemistry and Utilisation of Lignin), Izd.Zinatne, Riga, 1974, p.3.
30. O.P.Grushnikov and V.V.Elkin, "Dostizheniya i Problemy Khimii Lignina" (Advances and Problems in the Chemistry of Lignins), Izd.Nauka, Moscow, 1973, 296 pp.
31. F.E.Brauns and D.A.Brauns, "Chemistry of Lignin" (Translated into Russian from English), Izd.Lesnaya, Promyshlennost', Moscow, 1964, 864 pp.
32. V.M.Nikitin, "Lignin" (Lignin), Goslesbumizdat, Moscow–Leningrad, 1961, 316 pp.
33. N.I.Nikitin, in "Khimiya Drevesiny i Tsellyulozy" (The Chemistry of Wood and Cellulose), Izd.Akad. Nauk SSSR, Moscow–Leningrad, 1962, Chapter 22, 711 pp.
34. E.Adler, Symposium, "Khimiya i Biokhimiya Lignina, Tsellyulozy i Gemitsellyuloz" (The Chemistry and Biochemistry of Lignin, Cellulose, and Hemicelluloses), Izd.Lesnaya Promyshlennost', Moscow, 1969, p.180.
35. K.Freudenberg and A.C.Neish, "The Constitution and Biosynthesis of Lignin", Springer-Verlag, Berlin–Haaga–New York, 1968, 235 pp.
36. E.Adler, "Proccedings of the IVth International Congress of Biochemistry, Vienna, 1958", Pergamon Press, London–New York–Paris–Los Angeles, 1959, Vol.2, p.137.
37. J.C.Pew, V.Connors, and A.Kunishi, Symposium, "Khimiya i Biokhimiya Lignina, Tsellyulozy i Gemitsellyuloz" (The Chemistry and Biochemistry of Lignin, Cellulose, and Hemicelluloses), Izd.Lesnaya Promyshlennost', Moscow, 1969, p.107.
38. V.Connors, C.-L.Chen, and J.C.Pew, J.Org.Chem., 1970, **35**, 1920.
39. K.Forss and K.E.Fremer, Paperi ja puu paper ochträ, 1965, **47**, 443.
40. A.P.Lapan, V.A.Gordeeva, and V.G.Lavrent'ev, Symposium, "Khimiya i Ispol'zovanie Lignina" (The Chemistry and Utilisation of Lignin), Izd.Zinatne, Riga, 1974, p.87.
41. V.M.Reznikov, Khim.Drevesiny, 1969(4), 5.
42. K.Forss and K.E.Fremer, Paperi ja Puu Papper ochträ, 1965, **47**, 443.
43. K.Forss and K.E.Fremer, Tappi, 1964, **47**, 385.
44. J.A.Gargner and H.MacLear, Canad.J.Chem., 1965, **43**, 2421.
45. A.M.Kutnevich and V.M.Nikitin, Symposium, "Khimiya i Ispol'zovanie Lignina" (The Chemistry and Utlisation of Lignin), Izd.Zinatne, Riga, 1974, p.259.
46. M.F.Kiryushina and V.V.Tishchenko, "K Voprosu o Svyazi Lignina s Uglevodami v Drevesine. Materialy Sovetsko-Finskogo Simpoziuma" (The Problem of the Linkage between Lignin and Carbohydrates in Wood. Proceedings of the Soviet-Finnish Symposium), Leningrad, 1968, 4 pp.
47. N.F.Efendieva, O.P.Grushnikov, and M.N.Shorygina, Symposium, "Khimiya i Ispol'zovanie Lignina" (The Chemistry and Utilisation of Lignin), Izd.Zinatne, Riga, 1974, p.34.
48. B.D.Bogomolov and A.A.Sokolova, "Pobochnye Produkty Sul'fatno-Tsellyuloznogo Proizvodstva" (Side Products of the Sulphate-Cellulose Industry), Goslesbumizdat, Moscow, 1962, 436 pp.
49. F.Fischer, Sitzungber.Akad.Wiss.DDR.Math.Naturwiss. Techn., 1979(17), 26.
50. A.G.Michell, Austral.J.Chem., 1966, **19**, 2285.
51. H.Hatakeyama and J.Nakano, Cell.Chem.and Technol., 1970, **4**, 281.
52. R.W.Rex, Nature, 1960, **188**, 1185.
53. T.N.Kleinert and J.R.Marton, Nature, 1962, **196**, 334.
54. T.N.Kleinert, Pulp and Pap., 1964, **65**(7), T-275.
55. T.N.Kleinert, Pulp and Pap., 1966, **67**(6), T-299.
56. T.N.Kleinert, Tappi, 1967, **50**, 120.
57. C.Steelink, J.Amer.Chem.Soc., 1965, **87**, 2056.
58. C.Steelink, "Stable Free Radicals in Lignins and Lignin Products", Amer.Chem.Soc., Washington, 1966, Chapter 5.
59. K.P.Kringstadt. Tappi, 1970, **53**, 2296.
60. G.Domburgs and V.N.Sergeeva, "Sovremennye Metody Issledovaniya v Khimii Lignina, Materialy Vsesoyuznogo Seminara" (Modern Research Methods in the Chemistry of Lignin. Proceedings of the All-Union Seminar), Arkhangelsk, 1970, p.11.
61. E.G.Lyubeshkina, Abstract of Candidate's Thesis in Technical Sciences, Moscow Technological Institute for the Meat and Milk Industry, Moscow, 1966, 14 pp.
62. V.E.Gul', E.G.Lyubeshkina, M.S.Kurilo, and D.V.Ivanyukov, "Materialy Mezhdunarodnogo Simpoziuma po Makromolekulyarnoi Khimii" (Proceedings of the International Symposium on Macromolecular Chemistry), Publishing House of the Hungarian Academy of Sciences, Budapest, 1969, p.192.
63. M.S.Kurilo, Abstract of Candidate's Thesis in Technical Sciences, Mendeleev Moscow Institute of Chemical Engineering, Moscow, 1970, 14 pp.
64. L.T.Belova, Abstract of Candidate's Thesis in Technical Sciences, Moscow Technological Institute for the Meat and Milk Industry, Moscow, 1974, 26 pp.
65. E.G.Lyubeshkina, L.T.Belova, and V.E.Gul', "Tezisy Dokladov VI Vsesoyuznoi Konferentsii po Khimii i Ispol'zovaniyu Lignina" (Abstracts of Reports at the VIth All-Union Conference on the Chemistry and Utilisation of Lignin), Izd.Zinatne, Riga, 1976, p.146.

66. V.E.Gul', M.S.Kurilo, and E.G.Lyubeshkina, Vysokomol.Soed., 1970, **12A**, 1829.
67. L.T.Belova, E.G.Lyubeshkina, G.S.Markova, Yu.K.Ovchinnikov, and V.E.Gul', Vysokomol.Soed., 1973, **15A**, 2485.
68. V.N.Sergeeva, Symposium, "Khimiya Drevesiny" (The Chemistry of Wood), Izd.Zinatne, Riga, 1968, Vol.1, p.254.
69. G.E.Domburg, V.N.Sergeeva, G.A.Zheibe, et al., Symposium, "Khimiya i Ispol'zovanie Lignina" (The Chemistry and Utilisation of Lignin), Izd.Zinatne, Riga, 1974, p.349.
70. I.Kirsbaums, G.Domburgs, and V.N.Sergeeva, Symposium, "Khimiya i Ispol'zovanie Lignina" (The Chemistry and Utilisation of Lignin), Izd.Zinatne, Riga, 1974, p.359.
71. G.Domburgs, G.Dobele, T.E.Sharapova, and V.N.Sergeeva, Khim.Drevesiny, 1976(5), 64.
72. M.Kosik, G.Domburgs, V.N.Sergeeva, and A.Kalnins, "Khimiya Drevesiny" (The Chemistry of Wood), Izd. Zinatne, Riga, 1969, Vol.4, p.109; V.N.Sergeeva, G.Domburgs, and M.Kosik, "Khimiya Drevesiny" (The Chemistry of Wood), Izd.Zinatne, Riga, 1969, Vol.4, p.117; G.Domburgs, V.N.Sergeeva, and M.Kosik, "Khimiya Drevesiny" (The Chemistry of Wood), Izd.Zinatne, Riga, 1969, Vol.4, p.126.
73. M.Reti and J.Hosnoš, Vysk.pr.od boru pap.a celul., 1979, **24**, 45.
74. G.Domburgs, V.N.Sergeeva, and Z.Trops, "Khimiya Drevesiny" (The Chemistry of Wood), Izd.Zinatne, Riga, 1971, Vol.7, p.55.
75. M.V.Gritsai, E.I.Akhmina, S.I.Sukhanovskii, and B.B.Gakhenson, Symposium, "Khimiya i Ispol'zovanie Lignina" (The Chemistry and Utilisation of Lignin), Izd.Zinatne, Riga, 1974, p.156.
76. G.B.Izumrudova, L.N.Derevenchuk, F.I.Parashina, and N.N.Shorygina, Symposium, "Khimiya Drevesiny" (The Chemistry of Wood), Izd.Zinatne, Riga, 1968, Vol.1, p.323.
77. P.N.Odintsov, Symposium, "Voprosy Gidroliza, Khimii Drevesiny i Lesokhimii" (Problems of the Hydrolysis and Chemistry of Wood and Forest Chemistry), Izd. Akad.Nauk Latv.SSR, Riga, 1959, Vol.XVII, p.3.
78. K.A.Slavyanskii, V.I.Sharkov, and A.A.Liverovskii, "Khimicheskaya Tekhnologiya Drevesiny" (Chemical Engineering of Wood), Moscow, 1962, 572 pp.
79. S.I.Sukhanovskii, E.I.Akhmina, and A.V.Stepanova, Symposium, "Khimiya i Ispol'zovanie Lignina" (The Chemistry and Utilisation of Lignin), Izd.Zinatne, Riga, 1974, p.164.
80. A.N.Makler, M.N.Raskin, and M.I.Chudakov, Symposium, "Khimiya i Ispol'zovanie Lignina" (The Chemistry and Utilisation of Lignin), Izd.Zinatne, Riga, 1974, p.342.
81. V.F.Giterman, L.K.Stakhorskaya, M.N.Raskin, and M.I.Chudakov, Symposium, "Khimiya i Ispol'zovanie Lignina" (The Chemistry and Utilisation of Lignin), Izd.Zinatne, Riga, 1974, p.448.
82. V.A.Kosenko, L.V.Panasyuk, and V.G.Panasyuk, Symposium, "Khimiya i Ispol'zovnie Lignina" (The Chemistry and Utilisation of Lignin), Izd.Zinatne, Riga, 1974, p.207.
83. V.E.Bronovitskii, M.A.Volohkovich, L.L.Kalinskaya, and A.Nam, Uzbek.Khim.Zhur., 1968(3), 71.
84. A.N.Kazarnovskii and M.I.Chudakov, Uzbek.Khim. Zhur., 1974, 337.
85. M.I.Chudakov, V.I.Mal'tsev, and V.E.Bronovitskii, Gidrolizn.i Lesokhim.Prom., 1966(4), 13.
86. L.A.Pershina, V.M.Morozova, and V.P.Zhuchkov, Symposium, "Khimiya i Ispol'zovanie Lignina" (The Chemistry and Utilisation of Lignin), Izd.Zinatne, Riga, 1974, p.454.
87. Yu.A.Salimsakov, Candidate's Thesis in Technical Sciences, Tashkent Polytechnic Institute, Tashkent, 1975, 24 pp.
88. USSR P.116 082, 1958; Byul.Izobret., 1958(11), 54.
89. USSR P.812 910, 1979; Byul.Izobret., 1981(10), 100.
90. V.M.Selivanov and V.L.Levdikova, Symposium, "Khimiya i Ispol'zovanie Lignina" (The Chemistry and Utilisation of Lignin), Izd.Zinatne, Riga, 1974, p.421.
91. M.N.Tsypkina, R.K.Boyarskaya, and S.S.Vishnevskaya, "Khimiya i Izpol'zovanie Lignina" (The Chemistry and Utilisation of Lignin), Izd.Zinatne, Riga, 1974, p.309.
92. L.A.Grineva, L.N.Mozheiko, and V.N.Sergeeva, "Khimiya i Ispol'zovanie Lignina" (The Chemistry and Utilisation of Lignin), Izd.Zinatne, Riga, 1974, p.212.
93. R.K.Boyarskaya and M.N.Tsypkina, "Khimiya Drevesiny i Tsellyuzoly" (The Chemistry of Wood and Cellulose), Izd.Zinatne, Riga, 1968, Vol.1, p.243.
94. S.A.Sapotnitskii, "Ispol'zovanie Sul'fitnykh Shchelokov" (The Utilisation of Sulphite Liquors), Izd.Lesnaya Promyshlennost', Moscow, 1965, 283 pp.
95. T.Enkvist, Preprint of a Report at the Soviet-Finnish Symposium, Leningrad, 1968, 4 pp.
96. B.D.Bogomolov, Abstract of Doctoral Thesis in Technical Sciences, Kirov LTA, Leningrad, 1974, 72 pp.
97. P.P.Tiranov, Abstract of Candidate's Thesis in Technical Sciences, Riga, 1979, 26 pp.
98. E.D.Gel'fand, Abstract of Candidate's Thesis in Technical Sciences, IKHD, Academy of Sciences of the Latvian SSR, Riga, 1967, 18 pp.
99. A.D.Ivanenko, Abstract of Candidate's Thesis in Technical Sciences, Kirov LLTA, Leningrad, 1970, 22 pp.
100. K.V.Sarkanen, "The Chemistry of Wood" (Edited by B.L.Browning), Pergamon Press, New York, 1963.
101. B.D.Bogomolov, "Khimiya Drevesiny" (The Chemistry of Wood), Izd.Zinatne, Riga, 1968, Vol.1, p.157.
102. J.Marton, Tappi, 1964, **47**, 713.
103. E.I.Chupka et al., Symposium, "Khimiya I Ispol'zovanie Lignina" (The Chemistry and Utilisation of Lignin), Izd.Zinatne, Riga, 1974, p.264.
104. V.M.Reznikov, "Khimiya Drevesiny" (The Chemistry of Wood), Izd.Zinatne, 1969, Vol.4, p.5; M.Ya.Zarubin, A.M.Kutnevich, and A.B.Lukashenko, "Khimiya Drevesiny" (The Chemistry of Wood), Izd.Zinatne, 1974, Vol.15, p.76.
105. J.Zoldners, J.Surna, and J.Tirzina, Khim.Drevesiny, 1975(5), 116.
106. J.C.Westfahl, C.J.Carman, and R.W.Layer, "The 100th Meeting of the Division of Rubber Chemistry of the American Chemical Society, Cleveland, 1971", p.11.
107. V.V.Reznikov, B.D.Bogomolov, and O.M.Sokolov, "Khimiya Drevesiny" (The Chemistry of Wood), Izd. Zinatne, Riga, 1969, Vol.4, p.49.
108. Yu.S.Pilipchuk and V.I.Shufledovich, "Khimiya Drevesiny" (The Chemistry of Wood), Izd.Zinatne, Riga, 1969, p.93.
109. J.Marton and T.Marton, Tappi, 1964, **47**, 471.

110. J.T.Lindberg, "Assotsiatsiya, Rastvorimost' i Molekulyarnyi Ves Liginov. Materialy Sovetsko-Finskogo Simpoziuma" (The Association, Solubility, and Molecular Weight of Lignins. Proceedings of the Soviet-Finnish Symposium), Leningrad, 1968. 6 pp.
111. B.D.Bogomolov, O.M.Sokolov, N.D.Babikova, et al., Trudy ALTI (Arkhangelsk), 1971, **25**, 89.
112. B.D.Bogomolov, O.M.Sokolov, N.D.Babikova, et al., Trudy ALTI (Arkhangelsk), 1972, **32**, 64.
113. A.N.Pon'kina, Abstract of Candidate's Thesis in Chemical Sciences, LTITsBP, Leningrad, 1973, 20 pp.
114. C.Schuerch, J.Amer.Chem.Soc., 1952, **74**, 5061.
115. V.P.Svitel'skii, A.V.Obolenskaya, and V.N.Nikitin, Symposium, "Khimiya Drevesiny" (The Chemistry of Wood), Izd.Zinatne, Riga, 1968, Vol.1, p.189.
116. V.P.Svitel'skii, A.V.Obolenskaya, and V.M.Nikitin, "Sovremennye Issledovaniya v Khimii Lignina. Materialy Vsesoyuznogo Khimicheskogo Seminara" (Modern Research in the Chemistry of Lignin. Proceedings of the All-Union Chemical Seminar), Arkhangelsk, 1970, p.48.
117. M.S.Kukhnikova, S.F.Primakov, and E.V.Zagorul'ko, in "Khimiya i Tekhnologiya Tsellyulosy" (The Chemistry and Technology of Cellulose), Izd.Khimiya, Leningrad, 1976, No.3, pp.21.
118. A.M.Bukanov, I.A.El'kina, L.N.Larina, L.A.Belugina, and B.D.Bogomolov, "Tezisy Dokladov VI Vsesoyuznoi Konferentsii po Khimii i Ispol'zovaniyu Lignina" (Abstracts of Reports at the VIth All-Union Conference on the Chemistry and Utilisation of Lignin), Izd.Zinatne, Riga, 1976, p.171.
119. G.L.Chasovshchikov, F.F.Koshelev, et al., in "Polimery" (Polymers), Izd.Moskov.Gos.Univ., Moscow, 1965, p.414.
120. Z.G.Yudina, Abstract of Candidate's Thesis in Technical Sciences, Lomonosov Moscow Institute of Fine Chemical Engineering, Moscow, 1970, 24 pp.
121. D.P.Emel'yanov, V.G.Epshtein, N.L.Sergeev, et al., Symposium, "Khimiya Drevesiny" (The Chemistry of Wood), Izd.Zinatne, Riga, 1968, Vol.1, p.379.
122. Z.F.Suvorova, D.B.Boguslavskii, G.A.Blokh, B.D.Bogomolov, et al., Symposium, "Khimiya Drevesiny" (The Chemistry of Wood), Izd.Zinatne, Riga, 1968, Vol.1, p.385.
123. A.I.Ivanova, E.G.Kopylov, E.G.Lazaryants, B.D.Bogomolov, and E.D.Gel'fand, Symposium, "Khimiya Drevesiny" (The Chemistry of Wood), Izd. Zinatne, Riga, 1968, Vol.1, p.375.
124. B.D.Bogomolov, D.P.Emel'yanov, V.G.Epshtein, et al., "Sovremennye Metody Issledovaniya v Khimii Lignina. Materialy Vsesoyuznogo Seminara" (Modern Research Methods in the Chemistry of Lignin. Proceedings of the All-Union Seminar), Arkhangelsk, 1970, p.141.
125. L.B.Kosmodem'yanskii, E.P.Kopylov, D.P.Emel'yanov, and B.D.Bogomolov, "Tezisy Dokladov VI Vsesoyuznoi Konferentsii po Khimii i Ispol'zovaniyu Lignina" (Abstracts of Reports at the VIth All-Union Conference on the Chemistry and Utilisation of Lignin), Izd. Zinatne, Riga, 1976, p.172.
126. US P.2 906 718; Chem.Abs., 1960, **68**, 123 456.
127. A.D.Ivanenko, A.Z.Verkhovskaya, V.P.Svitel'skii, et al., Symposium, "Khimiya Drevesiny" (The Chemistry of Wood), Izd.Zinatne, Riga, 1968, Vol.1, p.367.
128. V.E.Gul', E.G.Lyubeshkina, and A.N.Shargorodskii, Mekhanika Polimerov, 1965(6), 3.
129. E.G.Lyubeshkina, R.V.Torner, and V.E.Gul', Mekhanika Polimerov, 1967(2), 200.
130. USSR P.184 432, 1963; Byul.Izobret, No.15, 87.
131. E.G.Lyubeshkina, O.N.Belyatskaya, N.A.Tarasova, L.T.Belova, et al., "Tezisy Dokladov Vsesoyuznoi Konferentsii po Primeneniyu Polimernykh Materialov v Pishchevoi Promyshlennosti, Kaliningrad, 1975" (Abstracts of Reports at the All-Union Conference on the Applications of Polymeric Materials in the Food Industry, Kaliningrad, 1975), p.19.
132. L.T.Belova, E.G.Lyubeshkina, N.N.Gorodetskaya, and V.E.Gul', "Tezisy Dokladov IV Vsesoyuznoi Konferentsii po Stareniyu i Stabilizatsii Polimerov" (Abstracts of Reports at the IVth All-Union Conference on the Ageing and Stabilisation of Polymers), Tashkent, 1976, p.69.
133. E.G.Lyubshkina, V.D.Feofanov, T.N.Muromova, et al., Plast Massy, 1975(9), 30.
134. V.I.Berezkin, Abstract of Candidate's Thesis in Technical Sciences, Mendeleev Moscow Institute of Chemical Engineering, Moscow, 1979. 16 pp.
135. V.I.Berezkin, E.G.Lyubeshkina, S.A.Vil'nits, and V.E.Gul', "Tezisy Dokladov Vsesoyuznoi Nauchno-tekhnicheskoi Konferentsii Protsessy i Apparaty Proizvodstva Polimerov, Metody i Oborudovanie dlya Pererabotki Ikh v Izdeliya" (Abstracts of Reports at the All-Union Science and Engineering Conference on the Processes and Apparatus in the Manufacture of Polymers. Methods and Equipment for Their Conversion into Finished Articles), Izd.MIKhM, Moscow, 1977, No.2, p.26.
136. V.I.Berezkin, E.G.Lyubeshkina, L.T.Belova, et al., Abstract of Symposium, "Ratsional'noe Ispol'zovanie Material'nykh Resursov" (Rational Utilisation of Material Resources), Izd.VINITI, Moscow, 1978, No.10.
137. V.K.Zavgorodnii and E.G.Lyubeshkina, "Tezisy Dokladov IV Vsesoyuznoi Nauchno-tekhnicheskoi Konferentsii po Voprosam Sozdaniya i Primeneniya Polimernykh Materialov v Otraslyakh Promyshlennosti, Proizvodyashchikh Produkty Pitaniya, Minsk, 1980" (Abstracts of Reports at the IVth All-Union Science and Engineering Conference on Problems of the Creation and Applications of Polymeric Materials in Branches of Industry Manufacturing Food Products, Minsk, 1980), p.118.
138. USSR P.854 957, 1979; Byul.Izobret., 1981(30), 111.
139. M.Beinoravicius, B.D.Bogomolov, L.Dambrauskas, et al., "Tezisy Dokladov VI Vsesoyuznoi Konferentsii po Khimii i Ispol'zovaniyu Lignina (Abstracts of Reports at the VIth All-Union Conference on the Chemistry and Utilisation of Lignin), Izd.Zinatne, Riga, 1976, p.153.
140. E.M.Cashell and B.J.McBrierty, J.Mater.Sci., 1977(12), 2011.
141. M.Jamroz and K.Kozlowsky, J.Polymer Sci., Polymer Chem., 1977, **15**, 1359.
142. V.Ya.Shlyapintokh, "Fotokhimicheskie Prevrashcheniya i Stabilizatsiya Polimerov" (Photochemical Reactions and Stabilisation of Polymers), Izd.Khimiya, Moscow, 1979, p.344.
143. V.V.Ershov, G.A.Nikiforov, and A.A.Volod'kin, "Prostranstvenno-Zatrudnennye Fenoly" (Sterically Hindered Phenols), Izd.Khimiya, Moscow, 1972, 352 pp.
144. V.D.Pokhodenko, "Fenoksil'nye Radikaly" (Phenoxy-Radicals), Izd.Naukova Dumka, Kiev, 1969, 196 pp.
145. E.G.Lyubeshkina, N.N.Pavlov, and V.E.Gul', Plast. Massy, 1967(7), 16.
146. USSR P.443 897, 1971; Byul.Izobret., 1974(35), 59.
147. O.N.Karpukhin, E.M.Slobodetskaya, and T.V.Magomedova, Vysokomol.Soed., 1980, **22B**, 595.

148. C.Sadrmohaghegh and G.Scott, Polymer J., 1980, **16**, 1037.
149. Yu.I.Khol'kin, in "Khimiya Drevesiny i Tsellyulozy" (The Chemistry of Wood and Cellulose), Izd.Zinatne, Riga, 1974, p.225.
150. R.B.Phillips, W.Brown, and V.Stannett, J.Appl. Polymer Sci., 1971, **15**, 2929.
151. R.B.Phillips, W.Brown, and V.Stannett, J.Appl. Polymer Sci., 1972, **16**, 1.
152. T.Koshijima and E.Muraki, J.Polymer Sci., 1968(6), 1431.
153. T.Koshijima amd E.Muraki, J.Jap.Wood.Res.Soc., 1964, **10**, 110.
154. C.Simionesku and J.Antan, Cell.Chem.Technol., 1969, **3**, 387.
155. A.F.Alksnis et al., Khim.Drevesiny, 1970(5), 115.
156. R.B.Phillips, W.Brown, and V.Stannett, J.Appl. Polymer Sci., 1973, **17**, 443.
157. J.Zoldners, J.Surna, and J.Tirzina, Khim.Drevesiny, 1975(5), 116.
158. J.Schurz, "The XXVIIth International Congress of Pure and Applied Chemistry. Plenary and Invited Lectures, Helsinki, 1979", Oxford, 1980, p.307.
159. V.N.Sergeeva, G.M.Telysheva, and L.I.Mozheiko, "XXII Mendeleevskii S'ezd po Obshchei i Prikladnoi Khimii. Referaty Dokladov i Soobshchenii" (The XIIth Mendeleev Congress on General and Applied Chemistry. Abstracts of Reports and Communications), Moscow, 1981, No.6, p.198.
160. US P.423 966 (1980); Chem.Abs., 1981, **89**, 654 321.

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