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METHOD OF PRODUCING WATER-SOLUBLE PRODUCTS FROM BLACK LIQUOR LIGNIN

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The present invention relates to a method for producing water-soluble products from black liquor lignin obtained by digesting hardwood, or coniferous wood, or other lignocellulose containing materials, according to the soda or sulphate cellulose processes.

It is known that the lignin sulphonic acid obtained as a by-product in the sulphite cellulose process has in many cases proved to be useful as an emulsifying and dispersing agent, and also for tanning and other purposes. A condition for this is amongst other things the solubility of the lignin sulphonic acid and its salts in water or diluted acids. Contrary hereto, it has hitherto not been possible to use waste lignin from the soda and sulphate cellulose processes, hereafter called black liquor lignin, for similar purposes, owing to lacking water-solubility of this lignin.

In our copending application, Ser. No. 201,695, filed December 19, 1950, we describe and claim a process of rendering black liquor lignin soluble in water and dilute acids. In this process black liquor lignin is treated with a sulfonating agent, such as sulfurous acid or a soluble sulfite, to introduce sulfonic acid groups into the aliphatic side chains of the lignin molecule. The water-soluble products thus obtained are useful for the above-mentioned and similar purposes.

It has been found that the sulfonating step of this acknowledged copending application can be facilitated and promoted by subjecting the black liquor lignin to an oxidizing treatment in connection with the sulfonation.

Based on these discoveries, according to the invention, the black liquor lignin is first subjected to an oxidizing treatment and then to a treatment with a sulphonating agent, such as sulphurous acid or a salt thereof, or a substance which can give rise to the formation of any of the mentioned compounds. It is also possible to carry out the oxidizing treatment and the sulphonation simultaneously. The black liquor lignin is not subjected to any preliminary special treatment with alkali before the conversion according to the invention and it may be used for this conversion directly in the form in which it is obtained by the digestion.

By means of the sulphonating treatment according to the invention which may be carried out in acid, neutral or, preferably, alkaline solution, the black liquor lignin is converted into sulphonic acid derivatives, the —SO_3H groups entering the aliphatic side chain of the lignin molecule, whereby water-soluble products are

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produced. As sulphonating agents preferably soluble sulphites are used, especially alkali metal sulphites and preferably sodium sulphite or, when working in acid solution, also sodium bisulphite, but also the corresponding ammonium salts.

The oxidizing treatment may be carried out with any suitable oxidizing agents, preferably oxygen or oxygen delivering substances, suitably in alkaline solution. Due to the oxidizing of the lignin, the subsequent conversion with a sulphite takes place more rapidly and may be carried out at a lower temperature. The oxidizing treatment may for example be accomplished by passing air or oxygen into a solution of the black liquor lignin at boiling temperature under normal pressure. If desired, the oxidation may be carried out in the presence of oxidation catalysts, such as salts of iron, copper and cobalt.

According to an embodiment of the invention the oxidizing and sulphonating treatment of the lignin material may be combined with a treatment with an aldehyde, preferably formaldehyde, or agents giving off aldehyde. This treatment with an aldehyde is carried out after the oxidizing treatment has taken place, but may be performed either before the sulphonating treatment—suitably in alkaline solution—or at the same time as the conversion with the sulphonating agent. In the former case —CH_2OH groups are introduced into the lignin molecule in the aromatic nuclei thereof, more precisely in positions that are in orthoposition to a free phenolic hydroxyl group. When subsequently reacting such methylol derivatives with a sulphite, preferably in a medium having a weak alkaline reaction, said —CH_2OH groups are converted into —CH_2SO_3H groups, and at the same time —SO_3H groups are introduced into the aliphatic side chain of the lignin molecule. These —CH_2SO_3H groups may also be formed in a single reaction stage, if the black liquor lignin—after the oxidizing treatment—is reacted with a mixture of formaldehyde and sodium sulphite.

Further, it is possible to combine said reactions with each other in such a manner that the black liquor lignin is first oxidized and simultaneously or afterwards subjected to a heating with a sulphite in acid, neutral or, preferably, alkaline solution, thus introducing —SO_3H groups in the aliphatic side chain of the lignin molecule, as indicated, whereupon the resulting product is reacted with an aldehyde, for example formaldehyde, in the presence of a sulphite,

preferably in alkaline solution, whereby —CH_2SO_3H groups are introduced into the aromatic nuclei of the molecule and at the same time the sulphonation in the aliphatic side chain is carried on to a still higher extent. A similar result is also obtained by first reacting the oxidized black liquor lignin with the aldehyde-sulphite mixture, for example formaldehyde-sodium bisulphite addition compound, and then subjecting the product thus obtained to a subsequent sulphonation by heating with a sulphite in acid, neutral or, preferably, alkaline solution.

When carrying out these combined reactions it is not necessary to isolate the product formed in the first conversion stage, but it may in many cases be suitable, after the first stage has been accomplished, to add directly to the reaction mixture the chemicals necessary for the second reaction stage, and then to carry out said reaction stage.

The treatment with the sulphonating agent, for example a sulphite, or a sulphite and an aldehyde (aldehyde-bisulphite addition compound), may for example be carried out within a temperature range of 50 to 200° C., suitably 80 to 170° C., preferably 100 to 160° C., when required under pressure. The quantity of sulphite used, calculated as anhydrous sodium sulphite, may be 10 to 100% of the quantity of anhydrous lignin, and the quantity of aldehyde may be equivalent to the quantity of sulphite or lower, down to about 1%, calculated on the quantity of the anhydrous lignin material. As already mentioned, the treatment is preferably carried out in alkaline solution in which case the sulphonation is accomplished in a shorter time, but in many cases it may also be to advantage to work in acid solution.

By applying the present invention, it is possible to produce from black liquor lignin sulphonic acid derivatives with varying content or number of sulphonic acid groups. Thus, when oxidizing and directly converting black liquor lignin with sulphite solutions at higher temperature, in accordance with the degree of acidity, the temperature and the time of reaction chosen, one or several SO_3H groups per 5 methoxyl groups are introduced into the lignin molecule. When reacting the oxidized black liquor lignin with an aldehyde, with simultaneous or subsequent treatment with a sulphite in the manner indicated, under formation of —CH_2SO_3H groups, likewise such a group enters per about 5 methoxyl groups.

Owing to the fact that direct sulphonation or sulphonation by formaldehyde-sulphite acts upon the lignin molecule at different places and by applying the first mentioned or the last mentioned of these two principal reaction types, or by combining said reaction types in different ways, as indicated above, it is possible to vary within wide limits the final content of sulphonic acid groups (SO_3H groups and CH_2SO_3H groups), in the reaction products, and as a consequence hereof also the properties of the products. Thus, for example, it has been proved that sulphonic acids, produced by oxidizing and converting black liquor lignin with formaldehyde-sulphite addition compound, are soluble in water and acetic acid, but they can be precipitated by dilute mineral acids. On the other hand, higher sulphonated products, which may be obtained for example by oxidizing and then reacting black liquor lignin first with formaldehyde-sulphite addition compound in a weak alkaline solution at 80° to 100° C. and then with a sulphite at a pH of 9 and about 130° C., are also soluble in dilute mineral acids, and are precipitated from their aqueous solutions only at a comparatively high concentration of mineral acid.

In this connection it may be pointed out that it is not necessary to use isolated, solid lignin products as starting material for the process. It is also possible to make use of the black liquor as such and to cause the lignin contained therein after oxidation to react at a suitable pH with a sulphite or formaldehyde-sulphite addition compound or with both, whereupon the sulphonated, water soluble lignin product thus produced is freed from the other constituents of the liquor, for example by dialysis.

The sulphonated lignin products produced according to the invention possess with regard to their composition a certain resemblance to the lignin sulphonic acids, which are obtained in the sulphite cellulose process. However, in several respects, characteristic differences exist between the two kinds of lignin sulphonic acids. The lignin sulphonic acids of the sulphite waste liquor are comparatively high-molecular—their average molecular weight is about 10,000—and they contain only very few phenolic hydroxyl groups. On the other hand, the sulphonic acids produced according to the present invention, are relatively low-molecular—their molecule weight is 1000–3000—and they contain in conformity with the starting material comparatively many free phenolic hydroxyl groups.

Owing to these properties, the sulphonic acid derivatives of black liquor lignin produced according to the invention are excellent tanning agents. Tanning tests have proved that they have a high affinity for the hide, and that they—contrary to lignin sulphonic acids from sulphite waste liquor—give a soft leather with increased shrinking temperature. Other purposes of utilization for which the products of the present invention are adapted are, for example, as emulsifying and dispersing agent, for example in the production of printing inks and cutting and drilling oils, as assistants in textile dyeing, as reinforcing fillers for caoutchouc and as dispersing, hardening-promoting and strength-increasing addition to cement.

Especially favourable results are obtained by employing black liquor lignin from the sulphate cellulose process, hereafter called "sulphate black liquor lignin," which to its character in certain respects is different from black liquor lignin obtained by digesting wood with solely alkali, the so-called "soda black liquor lignin." Owing to the presence of sulphides in the alkaline cooking liquor the lignin is dissolved from the wood more readily than is the case in the pure alkaline process ("the soda process"). This has been explained by the assumption that the sulphide present in the cooking liquor reacts with benzyl alcohol and benzyl ether groups in the lignin, converting them into mercaptan groups, part of which may subsequently be further converted, under the action of the alkali of the cooking liquor, into keto groups. In this way the highly reactive benzyl alcohol and benzyl ether groups mentioned are deactivated. In the soda process, however, these groups give rise to condensation reactions resulting in high-molecular lignin products which are removed from the pulp only by prolonged cooking with the alkaline liquor or by the use of a higher cooking temperature. The sulphate black liquor lignin may therefore be considered as a lignin product produced under milder conditions than the soda black liquor lignin and in accordance herewith sulphate black liquor

lignin reacts more readily with sulphites in the sulphonating process.

Another consequence of the condensation-preventing influence of the sulphide upon the dissolution of the lignin from the wood is that the sulphate black liquor lignin has a relatively lower and more uniform molecular weight than the soda lignin. Thus, the molecular weight of sulphate black liquor lignin is 1000–2000, consequently of the same order of magnitude as that of the most important vegetable tanning agents, and this fact may be a contributing cause to the especially good tanning properties which the water-soluble products produced from sulphate black liquor lignin according to the present invention have proved to possess.

Example 1

200 gs. sulphate black liquor lignin were dissolved in a solution of 32 gs. sodium hydroxide in 1 liter water and the solution was boiled for 12 hours under reflux while passing oxygen therethrough. After this treatment the lignin could be precipitated by acidifying with acetic acid. When analysed by potentiometric titration it proved to contain strong acid groups (sulphonic acid groups), although not in a sufficient quantity for obtaining the desired solubility in water and acids. In order to obtain a sufficiently high content of sulphonic acid groups, 50 gs. sodium sulphite (anhydrous) were added to the solution previously oxidized as described, whereupon the solution was heated for 3 hours at 150° C. The solution was then dialysed, until it was free from sulphite ions, and was thereupon evaporated. The product thus obtained contained 8.8% SO_3H and was readily soluble in water and dilute acetic acid. In order to obtain the same sulphonic acid content when using not previously oxidized sulphate black liquor lignin, it was necessary to use 100 gs. sodium sulphite, the conditions in other respects being analogous. The product had a high affinity for hide. Its content of tanning substance was 78%.

Example 2

A solution of 200 gs. sulphate black liquor lignin, 12 gs. sodium hydroxide and 70 gs. sodium sulphite (anhydrous) in 2 liters water was boiled for 8 hours under reflux while conducting air through the solution. The solution was then dialysed to be freed from salts, and thereupon evaporated. The product thus obtained contained according to potentiometric titration 7.5% SO_3H and was readily soluble in water and dilute acetic acid. If the reaction was carried out at the same temperature without conducting air through the solution, the lignin could be precipitated by acetic acid.

Example 3

50 gs. lignin product, produced according to Example 1, were heated for 6 hours at 100° C. in a solution of 50 gs. Na_2SO_3 and 25 ml. formaldehyde (40%) in 500 ml. water. The product obtained after dialysis and evaporation had a high content of sulphonic acid and could not be precipitated from its aqueous solution with dilute mineral acid.

Example 4

50 gs. lignin product, produced according to Example 2, were dissolved in 500 ml. sodium hydroxide (1%) and was reacted with 20 gs. formaldehyde-bisulphite addition product by heating for 6 hours at 100° C. The solution was worked up as in the preceding example.

Example 5

A solution of 200 gs. sulphate black liquor lignin and 20 gs. sodium hydroxide in 2 liters water was heated for 6 hours at 100° C. while conducting air through the solution. Hereupon 100 gs. formaldehyde-bisulphite addition compound were added, whereupon the solution—without conducting air therethrough—was heated for further 6 hours at 100° C.

What is claimed is:

1. In the manufacture of water-soluble products from lignin materials, the process which comprises sulfonating black liquor lignin by subjecting it to the action of a sulfonating agent, selected from the class consisting of sulfurous acid and water-soluble salts of sulfurous acid, also subjecting said lignin to an oxidizing treatment with an oxidizing gas, selected from the class consisting of air and oxygen, prior to completion of the sulfonating step, and recovering the resulting water-soluble sulfonated lignin product.

2. The process of claim 1 wherein the oxidizing treatment is conducted prior to the sulfonating treatment.

3. The process of claim 1 wherein the oxidizing treatment is conducted simultaneously with the sulfonating treatment.

4. The method of claim 1 wherein the oxidizing and sulphonating treatments are carried out in alkaline solution.

5. The method of claim 1 wherein the oxidizing treatment is carried out by conducting the oxidizing gas into an alkaline solution of black liquor lignin at boiling temperature.

6. The method of claim 1 wherein the sulphonating treatment is carried out at a temperature within the range of 50 to 200° C.

7. In the production of water-soluble products from lignin materials, the process which comprises subjecting black liquor lignin to an oxidizing treatment by contacting it with an oxidizing gas, selected from the class consisting of air and oxygen, and to a sulphonation, with an agent selected from the group consisting of sulfurous acid and water-soluble salts thereof, in combination with a treatment with an aldehyde, the oxidizing treatment being completed before the aldehyde treatment and prior to completion of the sulphonation.

8. The method of claim 7 wherein the black liquor lignin is first subjected to said oxidizing and sulphonating treatments and then to the treatment with an aldehyde.

9. The method of claim 7 wherein the black liquor is first subjected to said oxidizing treatment and then to said sulphonation whereupon the product thus obtained is reacted with an aldehyde.

10. The method of claim 7 wherein the black liquor is first subjected to said oxidizing and sulphonating treatments whereupon the product thus obtained is reacted with a mixture of a sulphonating agent and an aldehyde.

11. The method of claim 7 wherein the black liquor is first subjected to said oxidizing treatment and then reacted with a mixture of a sulphonating agent and an aldehyde whereupon the product thus obtained is subsequently subjected to a further sulphonation.

12. The method of claim 7 wherein the said aldehyde is formaldehyde.

13. The method of claim 7 wherein the oxidizing treatment is carried out in alkaline solution.

14. The method of producing water-soluble

lignin products suitable for use as tanning agents, emulsifying and dispersing agents, textile assistants, reinforcing fillers in caoutchouc and for similar purposes, which comprises oxidizing black liquor lignin, by contacting it with a gas, selected from the class consisting of air and oxygen, reacting the oxidized lignin at increased temperature with a sulphonating agent selected from the group consisting of sulphurous acid and water-soluble salts thereof, in order to introduce sulphonic acid groups into the lignin molecule, whereby the lignin is converted into water-soluble state, and then recovering the water-soluble lignin products thus obtained.

15. A method for producing water-soluble lignin products suitable for use as tanning agents, emulsifying and dispersing agents, textile assistants, reinforcing fillers in caoutchouc and for similar purposes, which comprises heating black liquor lignin while treating it simultaneously with an oxidizing agent, selected from the class consisting of air and oxygen, and a sulphonating agent selected from the group consisting of sulphurous acid and water-soluble salts thereof, reacting the product thus obtained with an aldehyde to produce water-soluble sulphonic acid derivatives of the lignin, and then recovering the water-soluble products thus obtained.

16. A method for producing water-soluble lignin products suitable for use as tanning agents, emulsifying and dispersing agents, textile assistants, reinforcing fillers in caoutchouc and for similar purposes, which comprises dissolving sulphate black liquor lignin in an alkaline solution of sodium sulphite, passing an oxygen-containing gas, selected from the class consisting of air and oxygen, through the solution at elevated temperature, heating the solution thus treated at a temperature within the range of 50 to 200° C. to convert the lignin into water-soluble sulphonic acid derivatives, and then recovering the water-soluble product thus produced.

17. A method for producing water-soluble lignin products suitable for use as tanning agents, emulsifying and dispersing agents, textile assistants, reinforcing fillers in caoutchouc and for similar purposes, which comprises dissolving black liquor lignin in an alkaline solution of sodium sulphite, boiling the solution under reflux to produce sulfonation of the lignin while passing an oxygen-containing gas, selected from the class consisting of air and oxygen, therethrough, adding formaldehyde to the solution,

heating the solution thus obtained to convert the lignin into water-soluble sulphonic acid derivatives, and then recovering the water-soluble products thus produced.

18. A method for producing water-soluble lignin products suitable for use as tanning agents, emulsifying and dispersing agents, textile assistants, reinforcing fillers in caoutchouc and for similar purposes, which comprises dissolving sulphate black liquor lignin in an alkaline solution of sodium sulphite, heating the solution while passing an oxygen-containing gas, selected from the class consisting of air and oxygen, therethrough, to convert the lignin into water-soluble sulphonic acid derivatives, and removing low-molecular water-soluble products present by dialysis.

19. A method for producing water-soluble lignin products suitable for use as tanning agents, emulsifying and dispersing agents, textile assistants, reinforcing fillers in caoutchouc and for similar purposes, which comprises mixing sulphate black liquor with an alkaline solution of sodium sulphite, heating the mixture while passing an oxygen-containing gas, selected from the class consisting of air and oxygen, therethrough, adding formaldehyde and again heating to convert the lignin into water-soluble sulphonic acid derivatives, removing low-molecular substances from the sulfonated products by dialysis, and then removing water-insoluble byproducts by filtration.

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