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(54) **Title:** METHOD OF PRODUCING LIGNIN WITH REDUCED AMOUNT OF ODOROUS SUBSTANCES

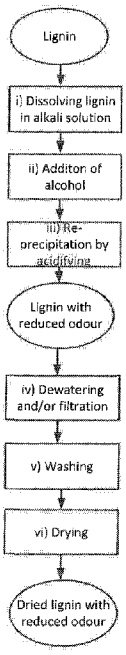

Fig. 2

(57) **Abstract:** The present invention relates to a method of producing lignin with reduced amount of odorous substances comprising the step of: • providing asolid phaselignin containing starting material to be contacted with a water solution comprising carboxylic acid; • dissolving the guaiacol andetylguaiacol content from the lignin into the water solution, and • draining off the water solution with its content ofguaiacol or etylguaiacol; • obtaining a lignin material with a reduced content of guaiacol or etylguaiacol The inventionalso relates to a lignin product with reduced odourobtained and/or obtainable by themethod obtained lignin as a component in polymer blends, anadditiveor filler in building materials, as binding agent in adhesives, and/or for the productionof a carbon fibre, especially in indoor applications.

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Method of producing lignin with reduced amount of odorous substances

TECHNICAL FIELD

The present invention relates to a method of producing or treating lignin in order to reduce its amount of odorous substances, to a lignin product obtained and to a use of the lignin product.

BACKGROUND ART

Lignin is a complex polymer occurring in certain plant walls making the plant rigid. Bonds linking lignin to cellulose are broken during a chemical pulping process. Lignin isolation from black liquor has been used during past years to provide lignin for commercial use, for example for use as a solid biofuel and dispersant. This lignin is also a valuable material for production of "green chemicals" and as a fuel for the production of chemicals. The production process of lignin of that kind is described for example in WO2006 /031 175. According to the process, lignin is separated from black liquor. The separation method may include steps to acidify the black liquor so that the lignin is precipitated. The solid phase is then separated from the liquor and can thereafter be cleaned or modified.

However, there is a desire to use lignin products also in other applications than fuel applications. The lignin product obtained by the isolation process is a renewable, non-poisonous environmentally friendly product which could be used for example as a raw material for building materials. However, the obtained lignin product suffers from a drawback of being malodorous, whereby the use of the product has been limited to few applications.

There is thus a great desire to reduce or eliminate the problems with odour in lignin products.

In the prior art, there have been attempts to reduce odour levels in lignin products.

WO 2012 /161 865 discloses a method in which pressurized black liquor may be reacted with an oxidizing agent, such as oxygen, peroxide or the like, in an amount sufficient to reduce or eliminate the odour level in the black liquor so that there will be little or no odour in the final lignin product. This step removes the odours by oxidating mercaptans (methyl, ethyl), and dimethyl, diethyl sulphides etc. However, with this process there is a risk that also lignin is oxidized and thus deteriorated or chemically modified.

There are still further documents related to pulping processes and treatment of lignin, e.g. in order to reduce impurities, such as WO 2014/116 150 and US 2016/137 680.

Even though there are prior art solutions for the reduction of odour levels, especially in respect of mercaptans, there is still a need for a process that removes also other organic odorous compounds effectively, and especially guaiacol and etylguaiacol. Guaiacol is a naturally occurring organic compound with an odour characteristic of aromatic compounds. The water solubility of guaiacol is limited to about 14-23 g/l at room temperature.

There is also a need for a process in which lignin is treated carefully such that its chemical structure and bondings remain to a large extent and in which lignin is not essentially fractionated by the odour reduction process. There is also need for an environmentally friendly process with a reduced risk for hazards in the production process. It is further an advantage if the dour reduction process can be integrated with lignin separation processes in a simple way.

SUMMARY OF THE INVENTION

The object of the present invention is to provide a method for reducing the amount of odorous substances in lignin products. It is also desired to provide a method for the production of a product in which lignin is treated carefully such that its chemical structure and bondings remain to a large extent and in which lignin is not severely fractionated due to odour reduction. It is also desired to provide a method for producing less odorous lignin products with a method that can result in high yield. It is also desired to provide a method which is environmentally friendly. Preferably could the method be used in connection with and/or integrated with available processes for separating lignin, i.e. the production of lignin products, as well as being able to be used for treatment of lignin in various forms after it has been separated and purified, e.g. in a pulping process.

The present method aims to address the above object and desires of producing or modifying lignin wherein lignin with reduced amount of odorous substances is obtained. The method is based on the idea of using a carboxylic acid in a water solution in order to be in contact with the lignin to be produced or treated. The lignin is present as solid matter, i.e. solid phase lignin containing material, which is mixed or washed with a carboxylic acid. This treatment may be performed during a pulping process when lignin is isolated or may be used for refined lignin.

The carboxylic acid used may preferably be acetic acid (common name) or ethanoic acid (IUPAC name).

The method for treatment of lignin in order to reduce the amount of odorous substances could be described as simple as including a step wherein solid state lignin is contacted with a solution comprising carboxylic acid. In a more detailed description, the method may be described as method for reducing at least the amount of guaiacol and etylguaiacol from the lignin which is characterized in that

said method comprises the step of:

- providing a solid phase lignin containing starting material to be contacted with a water solution comprising carboxylic acid;
- dissolving the guaiacol and etylguaiacol content from the solid phase lignin into the water solution (in tests, it has been verified that at least these compounds are dissolved into the carboxylic acid liquid phase), and
- draining off the water solution with its content of guaiacol or etylguaiacol;
- obtaining a lignin material with a reduced content of guaiacol or etylguaiacol

It has been shown in tests that a rather small addition of carboxylic acid drastically improves the reduction of guaiacol or etylguaiacol compared with simple water washing, and results in an almost odourless lignin.

One advantage by using treatment with carboxylic acid is that it is not necessary to dissolve the lignin if it is present in solid phase, e.g. precipitated lignin isolated from black liquor in an alkaline chemical pulping process. Hence, the process works for solid lignin, e.g. particulate lignin forming slurry with a carboxylic acid containing solution, as well as when lignin is dissolved in the carboxylic acid containing solution. To be noted, by solid state is meant that the lignin itself is in solid state but it may be in a liquid solution, e.g. particulate lignin in a solution together forming slurry. It has been found to function very well subjecting the solid phase lignin containing starting material to a displacement wash using the water solution comprising carboxylic acid in order to dissolve undesired impurities and at least guaiacol and etylguaiacol content from the lignin are solved into the water solution. The lignin containing starting material could in this case be an entire filter cake which is subjected to a displacement wash.

It has turned out that it has been beneficial in many ways to use carboxylic acid for washing solid state lignin in order to reduce odours. It seems like carboxylic acid has a high affinity for odorous compounds comprised in the lignin. When the solid lignin is being washed by carboxylic acid, it has turned out odorous compounds such as guaiacol and etylguaiacol dissolve surprisingly well in the carboxylic acid while leaving the lignin molecules themselves rather intact.

According to a preferred embodiment of the invention has the lignin containing starting material a dry matter content above 50 % (w/w), and a lignin content of this dry matter content exceeding 50% (w/w). To be noted, unless otherwise indicated are all percentages and relative proportions used herein meant to denote percentage or proportions by weight (w/w).

It is thus in particular advantageous to be able to use this method when lignin in solid state is present and still have a need for odour treatment since there is no need to dissolve the lignin once again. For example, if solid lignin from a lignin filter cake is used could the filter cake be disintegrated into smaller particles and located in a carboxylic acid containing water solution and thereafter dried once again. This could be easily done for a wet filter cake which may easily be disintegrated if placed in a solution; it may even be possible to merely stir the solution in a tank to make the filter cake be divided to rather small particles forming slurry. Alternatively, the filter cake could be washed with a carboxylic acid containing water solution when still on the filter. As still an alternative, a dry lignin filter cake could be immersed in a carboxylic acid water solution, either as one pieces or integrated into smaller blocks, or even mechanically treated to form smaller particles, so as to form slurry with the carboxylic acid containing solution. Hence, there are many ways in which the method may be advantageously used and it may be possible to maintain the lignin in solid phase and avoid dissolving the lignin and thus avoiding suspending and re-precipitating of solid lignin.

The solid state material to be used have preferably been prepared and purified to mainly comprise lignin such that the solid phase material have a lignin content above 80 %, more preferably above 90 % and most preferably above 95 % by weight. The method will work even if the relative amount of lignin is below 80 % by weight but there is less risk for negative interference by undesired solid components if there is high purity of lignin in the solid phase.

The solid starting material comprising lignin may for example be a filter cake which may be classified as dry or wet as described above.

The lignin may be mixed with the carboxylic acid containing water solution in a reaction tank. The lignin containing starting material is mixed with water and carboxylic acid in any order of mixing, and the resulting mixture is allowed to mature during a residence time of at least 5 minutes before draining off the water solution. The tank may be provided with some arrangement for stirring or for circulating the solution in order to improve the leaching or extraction process. In a non-limiting example, the residence time may for example be from 10 minutes up to 2 hours. The residence time needed to achieve a desired effect is dependent on for example the size of the particles, the stirring, the purity of the lignin and concentration of carboxylic acid in the solution/proportions of carboxylic acid and lignin. The temperature may also affect the desired retention time. However, the process works perfectly well at normal room temperature (18-25 degrees Celsius) but other temperatures could also be used. The process could for example include heating of the slurry/solution up to a temperature between 50 and 90 degrees Celsius. Concerning the size of the solid lignin in the process tank may it be between one extreme where one or several complete filter cakes are leached to the other extreme wherein the lignin is present as microscopic particles.

After the carboxylic acid treatment, the solution with solid particles, e.g. a slurry, is normally dewatered and filtrated such that there is a new filter cake built up, possibly followed by one or several drying steps.

The carboxylic treatment could also, in addition to or as an alternative, be used on a filter cake and by forcing a carboxylic acid containing liquid solution through the filter cake, e.g. in connection with washing or dewatering of the filter cake where the lignin containing starting material is subjected to a displacement wash using the water solution comprising carboxylic acid.

Even though it is described that the process is well suited for solid phase lignin it shall be noted that it also works well for lignin being dissolved and comprised in a carboxylic acid containing solution.

It may also be possible to mix the carboxylic acid containing solution to essentially pure lignin which has been liquefied by pressurizing and/or heating.

The amount of carboxylic acid to be used may be defined either as the concentration of carboxylic acid in the solution or the weight percentage of carboxylic acid to lignin. In general, a rather small amount of carboxylic acid is needed and a solution having 1% (w/w) of carboxylic acid may be enough. However, a higher concentration may decrease the time needed for removing the undesired components and if there are other components present as solid particles or in the solution, these impurities may interfere with the process and higher concentrations may be desired. Hence, it may be desired to use concentrations above 5 % (w/w) and even up to 30 %. Even though higher concentrations also function very well and even better from the aspect of removing the undesired components, such concentrations are often disregarded due to cost aspects and also a possible lowered yield of lignin after the treatment due to the high carboxylic acid concentration. However, there is no essential upper limit of the carboxylic acid concentration from the aspect of making the solution work. In the other end of the range, very low concentrations also shows an effect and undesired components are removed even if as low concentrations as 0,1 % (w/w) or lower is used. From 0.2 % there is a significant increase in the efficiency and already above 0.5 is the system working very efficient. Hence, concentrations of carboxylic acid of at least 0,1 % (w/w) in the solution is applicable, more preferred are concentrations from 0,2 preferred and for industrial use are appropriate concentrations in the interval of 0,1 to 30 % (w/w), preferably between 0,2 to 20 % (w/w) and in most cases is 0,5 – 10 % (w/w) desired.

The amount of carboxylic acid could also be defined in relation to the amount of lignin to be treated. Low concentrations of the carboxylic acid containing solution may not be appropriate to use if the total amount of lignin is comparatively high to the amount of solution used, in particular if the solid phase lignin is of low purity and the process may be disturbed by contaminants. In general, it is desired to have a proportion of carboxylic acid: lignin in which the amount of carboxylic acid is more than 1:200, in general more than 1:100 and in most cases more than 1:50. A suitable proportion which is used with adequate results is 1:10. There may of course be even higher concentrations and a proportion of 1:3 or even 1:1 may work efficiently but in general is it desired to keep the relations lower in order to reduce the amount of

carboxylic acid used in order to reduce costs and unnecessary additional processing time in regaining the acid. By using a proportion of carboxylic acid to lignin in which the amount of carboxylic acid is less than 1:3 will in general provide for an extraction of the odorous substances while lignin in itself is not affected too much. Thus, lignin is substantially not fractionated due to carboxylic addition and a high yield of lignin can still be obtained.

The carboxylic acid is preferably acetic acid or a c1-c2 carboxylic acid, e.g. methanoic acid or ethanoic acid. Higher carbon chain carboxylic acids may also be used but are generally considered to be less common to use due to they are in general less common and more expensive. However, they would also work in the same way if used in the process and reduce the amount of undesired substances.

The carboxylic acid may also be combined with and addition of an alcohol that also promotes dissolution of guaiacol or etylguaiacol.

The odour free lignin produced can thus be used as such for different applications such as filler for building and construction materials, also aimed for in-house applications due to the reduced or eliminated odour.

The lignin containing starting material can be lignin isolated from black liquor in an alkaline chemical pulping process. The black liquor can be soda or kraft black liquor.

The lignin containing starting material can be obtained from a process comprising the steps of:

a) precipitating lignin by acidifying black liquor obtained from the alkaline chemical pulping process;
b) dewatering and/or filtrating the obtained lignin to provide a filter cake;
c) re-suspending the lignin;
d) adjusting the pH of the obtained suspension in step c) to a pH lower than 6;
e) dewatering and/or filtrating the acidic suspension from step d) to provide a filter cake; and
f) washing and dewatering the filter cake.

Preferably, pH in step d) is adjusted to be lower than 4, such as equal with or lower than 3.5, e.g. 2-2.5, so that as much lignin as possible is re-suspended and thus a high yield and good filtration properties in the following filtration operations e) and f) can be obtained.

Prior to the step a), the process may comprise a pre-step in which black liquor is fractionated by filtration by for example membrane filtration such as micro- and ultra-filtration. By the mechanical separation it is possible to separate for example particulate material, hemicelluloses and/or it is possible to mechanically fractionate lignin and to obtain a specific fraction of lignin. In this way it is possible to obtain at least partially purified starting material and/or lignin fraction while high yield can be obtained since lignin is not substantially chemically affected. Another way to achieve fractions of lignin is a fractionation by means of different pH levels and select lignins from a certain pH-window for further processing.

Herein, by a filter cake is meant a filter cake comprising or consisting of lignin and with dry matter content above 50% and lignin content above 50% of this dry matter content. The washed filter cake can be directly used in step i) above, and the method of producing lignin with reduced odour, i.e. the odour-treatment, can be integrated into the process for obtaining lignin from black liquor. In this way energy savings are possible, since lignin needs not to be dried before the odour treatment. However, it is also possible to dry the lignin as a last step in the process for obtaining lignin, wherein the process further comprises the step of:

g) drying the filter cake

By dewatering and drying the filter cake it will be easy to transport and thus for example the odour treatment can be made in another factory.

To further increase odour reduction the process for obtaining lignin, also called for lignin separation or isolation process, can also comprise the step of adding a carboxylic acid prior to, during or after precipitation in step a), and/or adding a carboxylic acid prior to, during or after at least one of the dewatering and/or washing steps b), c), e) and f) to reduce the amount of odorous substances. It is in particular adequate to add carboxylic acid at some time after the pH-adjusting step, either in any of the steps c, e or f in the lignin obtaining process or in an additional step or process after these steps. The carboxylic acid may suitably be used together

with another acid such as sulfuric acid in steps c,) e) and f). By the addition of carboxylic acid during the lignin separation, the odour reduction may be further improved.

The carboxylic acid can be added in the process in an amount as previously disclosed. From the point of view of desiring a high yield of lignin, whereby lignin not is severely affected, and essentially no fractionation of lignin is occurred may the higher ranges of the intervals for the carboxylic acid concentration be avoided while from the point of view of extracting undesired content in the lignin may it be desired to avoid the lower ranges of the carboxylic acid concentrations disclosed. Hence, depending on the desired yield and purifying efficiency, a suitable carboxylic acid concentration could be selected.

Lignin in step i) obtained from kraft pulping process may suitably be used. Kraft pulping process has been found to be especially suitable for lignin separation, as disclosed e.g. by "Tomani, Per; The Lignoboost Process; Cellulose Chem Technol., 44(1.-3), 53-58 (2010).

The present method of producing lignin with reduced amount of odorous substance have been tested to result in yield which is over 80%by weight, based on the weight of the lignin containing starting material before the treatment, and even over 85%. Thus, the method leads only to minor material losses.

The odorous substances that are extracted with the present method comprise at least guaiacol or etylguaiacol, but preferably also any residual content of at least one of dimethyl sulphide, dimethyldisulphide, dimethyltrisulphide, dimethyltetrasulphide, and other phenolic compounds. In tests the content of guaiacol or etylguaiacol has been used to verify the functionality of the cleaning process

However, all these substances listed above cause very bad odour which has made lignin products difficult to use in indoor applications. Also other odorous substances, e.g. organic substances having low concentrations, can be extracted by means of the present method. The concentrations of the odorous substances in form of guaiacol or etylguaiacol have been proved to be reduced by at least 50%, the concentration being calculated from a peak area of a respective peak in a chromatogram. Preferably, the concentration of the odorous substances in form of guaiacol or etylguaiacol is reduced by at least 70%, and typically well above 93% and up to 97%.

The method also preferably comprises at least partially recirculating the carboxylic acid back into process and thus cost savings can be obtained while the process can be made more environmentally friendly.

Preferably, the carboxylic acid is ethanoic acid. Ethanoic acid effectively dissolves organic malodorous substances, and especially guaiacol dissolves better in ethanoic acid than in other carboxylic acids whereby the use of ethanoic acid is especially advantageous.

The present invention also relates to a lignin product with reduced odour obtained and/or obtainable by the above-defined method. The method enables a yield of the obtained lignin which is more than 80% by weight, based on the weight of the lignin containing starting material before steps I)-iii). Also, the concentration of the odorous substances in the obtained lignin product is at least 50% less and preferably less than 70% than in a corresponding untreated lignin, the concentration being calculated from a peak area of a respective peak in a chromatogram. Thus, the odour problems in connection with lignin products have been reduced substantially.

The present invention also relates to use of the lignin product as defined above as a component in polymerblends, additive or filler in building materials; as binding agent in adhesives, and/or for the production of a carbon fibre. The lignin product can also be used in building and construction materials that are intended for use indoors. Further application areas are for example manufacturing of fibre boards, car panels, as a cross-linking agent in vehicle tyres, as antioxidants and as UV-protectors. The application areas are not limited to the above-mentioned areas, other application areas are possible.

Further objects, features and advantages of the present invention will be described with reference to the detailed description below and to the appended drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows a flow chart illustration of the method according to the invention;

Fig.2 shows a flow chart illustration of an example method according to the present invention; and

Fig. 3 shows a flow chart illustration of a process for lignin isolation using the Lignoboost™ process;

Fig.4 shows how the inventive addition of carboxylic acid, here in form of HAc, may be added already into the Lignoboost™ process.

DETAILED DESCRIPTION

In the method of the present invention, which is schematically illustrated in a flow chart in Fig 1, is lignin treated to obtain a lignin product with reduced odour. By "lignin" is meant any lignin, which may be pure lignin or lignin with small amounts of impurities, and with dry matter content above 50% and more than 50% of this dry matter content being lignin, also referred to isolated lignin. According to the present method, the amount or concentration of the odorous substances can be reduced in lignin products while it is possible to obtain high yield of lignin. The less odorous or substantially odourless lignin product can be used in a wide range of applications including indoor applications which is a huge advantage.

Lignin to be treated by the present method is according to one aspect obtained as a by-product from an alkaline chemical pulping process. The alkaline chemical pulping process may be sulphate, also called kraft, process or soda process. Both processes result in alkaline material by cooking the fibre-based material in white liquor at a cooking temperature of from about 130-200'C to make lignin soluble in the cooking liquor. White liquor is a mixture of sodium hydroxide and sodium sulphide. By black liquor is meant the cooking liquor obtained during cooking from the alkaline chemical pulping process. Black liquor contains residues of white liquor and other pulping chemicals, lignin, hemicelluloses and other extractives from the fibre-based material. Even though the process is exemplified by the above processes may lignin isolated by any process be used in this method, in most cases could the lignin also be treated during the process itself.

The fibre-based material from which the isolated lignin is extracted can be softwood, hardwood or non-wood, such as annual plants. The softwood tree species can be for example, but are not limited to: spruce, pine, fir, larch, cedar, and hemlock. Examples of hardwood species from

which pulp useful as a starting material in the present invention can be derived include, but are not limited to: birch, oak, poplar, beech, eucalyptus, acacia, maple, alder, aspen, gum trees and gmelina. Preferably, the fibre-based material mainly comprises softwood. The fibre-based material may comprise a mixture of different softwoods, e.g. pine and spruce. The fibre-based material may also comprise a non-wood raw material, such as bamboo and bagasse. The fibre-based material may also be a mixture of at least two of softwood, hardwood and/or non-wood. Hence, the origin of the lignin is of less importance and the method should be useful for any lignin regardless of its origin.

The amount of odorous or odour containing substances can be reduced in the lignin product by means of extracting. Especially, organic malodorous substances can be extracted by the present method. Extracting is suitably selective, meaning that substantially mainly the odorous or odour containing substances are extracted. The extraction is obtained by means of the addition of carboxylic acid to a water solution, slurry or a solid body comprising lignin. The odorous substances are extracted in or leached by carboxylic acid, preferably methanoic acid or ethanoic acid, in order to remove odorous substances from the lignin. The amount of the carboxylic acid to be added should be kept at a sufficiently low level to avoid that lignin is seriously affected. In general, the amount of carboxylic acid to be added is less than 30%, and the amount may suitably be 0.2 to about 20%, based on the dry weight of lignin. As previously discussed, the amount of carboxylic acid could be decided based on the desired level of purification and not use more than needed to reach this level. The carboxylic acid including the extracted odorous substances is removed from the process and optionally recirculated at least partly back in the process.

Reference is now made to Fig. 2 in which the method according to the present invention is schematically illustrated more in detail

The lignin is preferably slurried in water in stage i), and thereafter is carboxylic acid (HAc) added in step ii), However the method also works if HAc is mixed into the water before adding to the lignin. In step iii) may also optionally alcohol (EtOH) be added to the water or lignin slurry. The method may comprise a maturing period of desired length that should last for at least 5 minutes, preferably at least 30-60 minutes, or even longer if sufficient storage volume is

available. . The maturing period can be adjusted by the skilled person to different processes and needs. Depending on the state of the lignin, the maturing may be desired to continue for different times. In case the lignin is dissolved in a solution a shorter time may be needed compared to if the lignin is present as particles, e.g. from a dissolving a wet filter cake. In case the lignin is present as even larger entities, e.g. as a solid, dry filter cake or larger particles, could even longer time be desired to partly disintegrate the larger entities and/or allowing the carboxylic acid to be better soaked into the solid matter and to enable a more efficient leaching operation.

After leaching is the slurry dewatered obtaining a lignin product with fewer odours, and explicitly with a substantial reduction in guaiacol and/or etylguaiacol.

The lignin cake obtained after dewatering or filtering will have a reduced concentration of odorous substances after this treatment. However, in most applications the lignin may need washing and drying if desired. Dewatering can be performed by any means to withdraw water. For example, the dewatering is performed by using centrifugation, a filter press apparatus, a band filter, a rotary filter, such as a drum filter, or a sedimentation tank, or similar equipment. Filtration can be performed by using any conventional apparatus suitable for filtration, such as filter press or a band filter. The filtrate from the dewatering step can be re-circulated to a recovery system, and the carboxylic acid can be further recirculated back in the process.

Subsequent to dewatering and/or filtration, the obtained lignin in the form of a filter cake is washed in step iii). Washing can be performed by using water and/or small amounts of carboxylic acid, e.g. 0.5-10% by weight based on the weight of lignin, such as ethanoic acid. Also during the wash, it is advantageous if the pH is kept acidic, such as from pH 1.5 to pH 5, preferably from pH 1.5 to pH 3.5. In this way the yield of lignin can be further increased. After washing, the obtained filter cake is dried in step iv) and a final lignin product with reduced odour is obtained.

Lignin to be treated according to the present invention can be obtained from a process for separation or isolation of lignin, which is illustrated in the flow chart of Fig. 3 and which is also commercially called for LignoBoost™ process, and Fig.4 illustrates how the Lignoboost process may be boosted by optionally adding HAc in differing process positions. In step a) of the process lignin is precipitated from alkaline black liquor by acidifying black liquor obtained from an

alkaline chemical pulping process. The chemical process is preferably kraft process. Acidifying can be performed by any means sufficient to acidify black liquor. Preferably the acidifying is performed by adding CO_2 to said black liquor in a carbonating stage. Carbon dioxide is the preferred alternative since this acid may be obtained from the pulp mill in form of exhaust gases from the lime kiln. By using carbon dioxide in step a) so as to acidify the black liquor approximately to a pH between 11.5 and 9, normally around pH 10, a lignin product can be obtained, and the filtrate obtained from subsequent dewatering is still alkaline and may be sent to the black liquor evaporation train in the recovery island without changing the pH level of the black liquor flow to said evaporators.

In stage (c) the dewatered lignin filter cake (still alkaline) is resuspended in an acidic slurry using H_2SO_4.

The lignin product can be used as fuel or for the production of chemicals and has reasonably low ash content and a low tendency to cause corrosion.

Prior to step a), the process optionally comprises a pre-step in which black liquor can be filtrated for example by membrane filtration. By this mechanical separation it is possible to separate for example particulate material, hemicelluloses and/or it is possible to mechanically fractionate lignin and to obtain a specific fraction of lignin. Another way to achieve fractions of lignin is fractionation by different pH levels and select lignins from a certain pH-window for further processing. In this case may of course carboxylic acids also be used, together with other acids, which may improve the overall efficiency in removing odorous substances from the lignin.

In the step b) as illustrated in the flow chart, the obtained lignin is dewatered and/or filtrated in a first dewatering and/or filtration step. Also in this connection the dewatering may be performed by any means to withdraw water, for example by using centrifugation, a filter press apparatus, a band filter, a rotary filter, such as a drum filter, or a sedimentation tank, or similar equipment. For example, when using a filter press apparatus the filter cake obtained through dewatering may be blown through by gas or a mixture of gases, preferably compressed air in order to dispose of the remaining liquid, such as black liquor, before resuspending the obtained cake as set out in step c). The filtrate from the dewatering step can be re-circulated to the pulp mill black liquor recovery system. The pH level adjustment before dewatering/filtration, made

by addition of acid preferably CO2 (g), can be combined with an adjustment of ion strength, preferably by using alkali metal ions or multivalent alkaline earth metal ions, most preferred calcium ions. Higher ion strength gives at a given pH lower yield losses of lignin as the lignin becomes more stable. Even though it is a dewatering step could small amounts of carboxylic acid be used during this step (see Fig.4), e.g. in the end of or after the dewatering step.

As the first Lignoboost™ product produced was in form of fuel pellets, a reduction of inorganic content was needed as such content could cause corrosion in power boilers. Thus, the step c) comprises re-suspending the lignin to form an acidic suspension by adding H_2SO_4. Generally, by a suspension is meant a heterogeneous mixture containing liquid-and small solid particles, such as about 1 µm or larger. The particles in the suspension are able to settle whereby it is possible to obtain a filter cake. Also in this step carboxylic acids could be used to increase removal of odorous substances.

In the step d), the pH level is preferably adjusted to below approximately pH 6, and suitably below approximately pH 4, and preferably below 3.5, e.g. 2-2.5. The pH level is preferably from pH 1.5 to pH 3.5 to ensure that substantially all lignin is re-suspended and to give good filtration properties in the following dewatering filtration step. It is also important in order to isolate a lignin with low content of inorganics. The acidic conditions establish an efficient leaching of metal ions from the lignin. Acidifying can be performed with the same chemicals as in connection with acidifying black liquor and as described above. Carboxylic acids could thus be used herein, possibly together with other acids.

After acidifying, a second dewatering and/or filtration step e) is performed similarly as the above-defined step b). Carboxylic acid could be used also during this step.

In step f), the obtained filter cake is washed and the washing liquid, such as acidified water, can have a pH level of below approximately pH 6, preferably below approximately pH 4. The pH level is most preferred a pH from 1.5 to 3.5. The washing liquid is dewatered and in one embodiment of the invention, the obtained filter cake is treated with the method steps I)-iii) without drying the filter cake before the treatment. This step is suitable to be performed in the presence of carboxylic acids in the washing liquid.

In general, the positive effect of using carboxylic acid treatment in the process above defined by steps a) to f) is probably most efficient if it is used in connection with steps e) and f).

According to another embodiment the method further comprises the step g) of drying the filter cake, whereby the filter cake can be easily e.g. transported.

The filter cake obtained from the final dewatering step above, in connection with the method of treating lignin to reduce odorous substances, either dried in the optional drying step g) or not, may thus be used for the carboxylic acid treatment described in figures 1 and 2. It is to be noted that the acidic reslurrying in stage c and d in the Lignoboost process do not effectively reduce content of guaiacol or etylguaiacol.

With the present method of producing lignin with reduced amount of odorous substances it is possible to obtain high yield, such as over 80% by weight, based on the weight of the isolated start lignin. Even higher yields are possible, such as over 85% and up to about 90-95%. Thus, the method leads only to minor material losses which are a major advantage. The high yield can be obtained due to the fact that the extraction method is rather moderate meaning that substantially no fractionation of the lignin occurs due to odour reduction process. Mainly only odorous substances, especially organic odorous substances, are extracted, and the cleaning process may be validated by measuring the content of guaiacol and etylguaiacol before and after the cleaning process using spectrum analysis. The odorous substances that are extracted with the present method comprise at least guaiacol and etylguaiacol but also one of dimethyl sulphide, dimethyldisulphide, dimethyldisulphide, dimethyltetrasulphide, and other phenolic compounds. These substances lead to malodourous gases which have made lignin products difficult to use in indoor applications. The concentration of the odorous substances may be reduced by at least 50%, the concentration being calculated from a peak area of a respective peak in a chromatogram. Preferably, the concentration of the odorous substance is reduced by at least 70%. Thermogravimetry analysis (TGA) of the lignin product produced by the present process shows that the lignin is essentially not affected by the present process. This further supports the conclusion of the present invention that the present process is gentle towards lignin, while the odorous substances can be reduced effectively.

Due to the obtained odour reduction, the lignin product is possible to use in many applications. For example lignin can be used as a component in polymer blends, an additive or filler in building materials, as binding agent in adhesives, and/or for the production of a carbon fibre. The lignin product can also be used in building materials that are intended for use indoors. Further application areas are for example manufacturing of fibre boards, as a crosslinking agent in vehicle tyres, as antioxidants and as UV-protectors. The application areas are not limited to the above-mentioned areas, other application areas are possible.

The invention is further described in the following example.

Example

Similar test has been performed as detailed in previously filed SE1451641-3(hereby incorporated by reference), having a filing date of Dec 22, 2014. In SE1451641-3 has been tested to clean lignin obtained from the LignoBoost™ process, using a process where the lignin is first dissolved in an alkaline solution, adding a 1% (on weight) of EtOH, followed by an additional acidification until lignin precipitates again.

In the tests performed according to the invention the same Lignoboost lignin is simply leached in a water solution with a small charge of HAc (1% on weight) reaching a reduction of guaiacol in the same order as with the cleaning tests of SE1451641-3. This is performed without extra charge of alkali for dissolution of the lignin, and extra charge of acidifier to precipitate lignin again. Thus a rather modest charge of 1% HAc in a water solution obtains a yield of 95% odour free lignin, and the leaching do not affect the physical, chemical or mechanical properties of the odour free lignin produced.

CLAIMS:

1. Method for treatment of lignin in order to reduce the amount of guaiacol and etylguaiacol from the lignin
characterized in that
said method comprises the step of:
   - providing a solid phase lignin containing starting material to be contacted with a water solution comprising carboxylic acid;
   - dissolving the guaiacol and etylguaiacol content from the lignin into the water solution, and
   - draining off the water solution with its content of guaiacol or etylguaiacol;
   - obtaining a lignin material with a reduced content of guaiacol or etylguaiacol.
2. A method according to claim 1 wherein the lignin containing starting material has a dry matter content above 50 % (w/w), and a lignin content of this dry matter content exceeding 50 % (w/w).
3. A method according to claim 1 or 2 wherein the lignin containing starting material is mixed with water and carboxylic acid in any order of mixing, and the resulting mixture is allowed to mature during a residence time of at least 5 minutes before draining off the water solution.
4. A method according to claim 1 or 2 wherein the lignin containing starting material is a filter cake subjected to a displacement wash using the water solution comprising carboxylic acid.
5. A method according to any previous claim wherein the content of carboxylic acid in the water solution is in the range of 0.1-50% by weight.
6. A method according to claim 5 wherein the content of carboxylic acid in the water solution is in the range of 0.5-10% by weight.
7. A method according to claim 6 wherein the content of carboxylic acid in the water solution is below 5% by weight.
8. A method according to any of previous claims 5-7 wherein the carboxylic acid content is an acetic acid.
9. A method according to any of previous claims 5-7 wherein the carboxylic acid is a methanoic acid or ethanoic acid
10. A method according to any of previous claims 5-7 wherein the carboxylic acid content is combined with an addition of an alcohol.

11. A method according to any previous claim characterised in that the carboxylic acid containing liquid phase solution also comprises another acid.

12. A method according to any of the preceding claims wherein the lignin containing starting material is obtained from a process comprising the steps of:

    i. precipitating lignin by acidifying black liquor obtained from the alkaline chemical pulping process;

    ii. dewatering and/or filtrating the obtained lignin to provide a first filter cake;

    iii. re-suspending the lignin;

    iv. adjusting the pH of the obtained suspension in step c) to a pH lower than 6;

    v. dewatering and/or filtrating the acidic suspension from step d) to provide a second filter cake; and

    vi. washing and dewatering the second filter cake; whereby the lignin containing starting material is obtained.

13. Lignin product obtained and/or obtainable by the method according to any one of claims 1-12.

14. Lignin product according to claim 13, wherein the concentration of guaiacol and etylguaiacol in the obtained lignin product is at least 50% less than in the lignin containing starting material, the concentration being calculated from a peak area of a respective peak in a chromatogram.

15. Use of the lignin product according to any of claims 13 or 14 as a component in polymer blends, an additive or filler in building and construction materials, as binding agent in adhesives, and/or for the production of a carbon fibre.

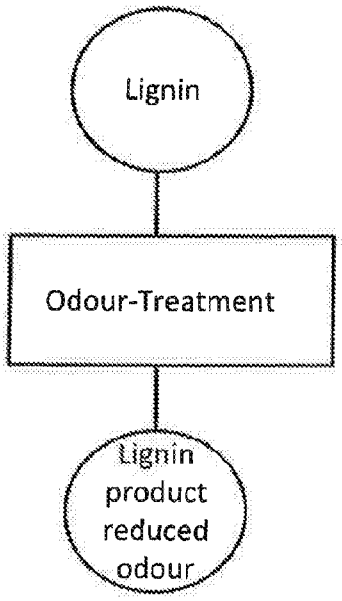

Fig. 1

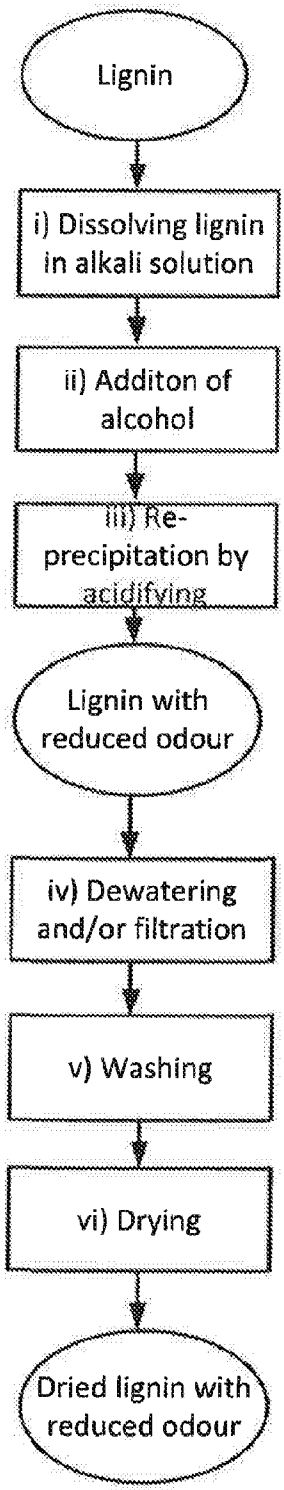
Lignin
i) Dissolving lignin in alkali solution
ii) Additon of alcohol
iii) Re-precipitation by acidifying
Lignin with reduced odour
iv) Dewatering and/or filtration
v) Washing
vi) Drying
Dried lignin with reduced odour
Dissolving lignin in water

Fig. 2

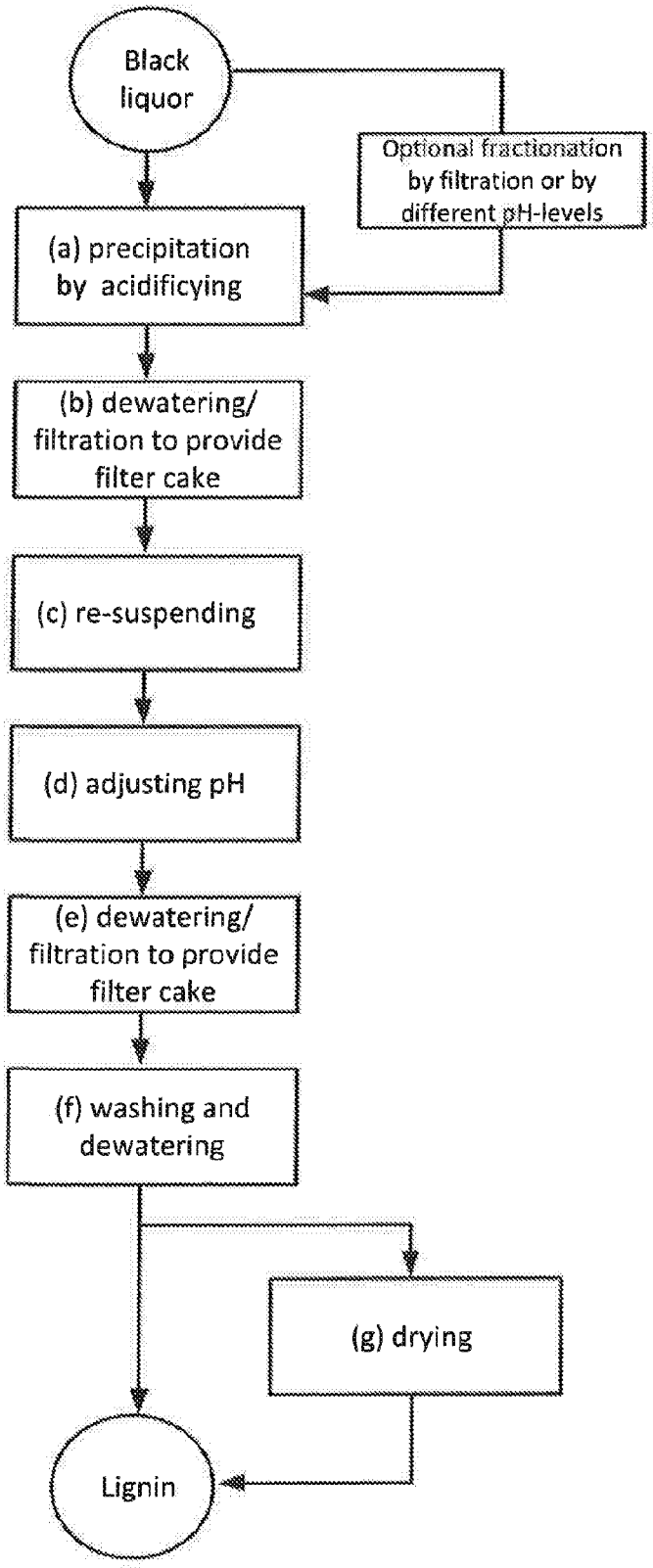
Black liquor
Optional fractionation by filtration or by different pH-levels
(a) precipitation by acidificying
(b) dewatering/ filtration to provide filter cake
(c) re-suspending
(d) adjusting pH
(e) dewatering/ filtration to provide filter cake
(f) washing and dewatering
(g) drying
Lignin

Fig. 3

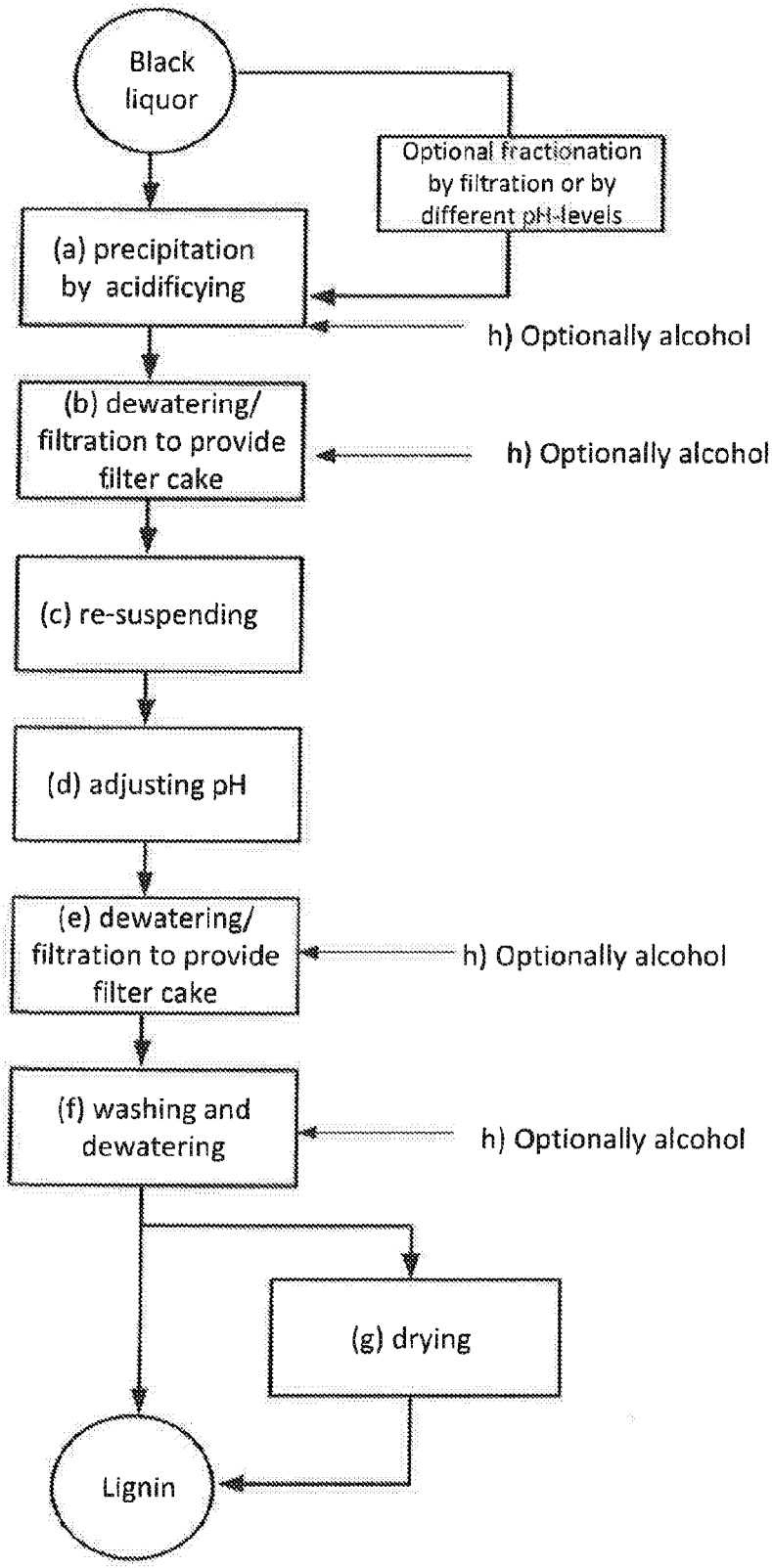
Black liquor
Optional fractionation by filtration or by different pH-levels
(a) precipitation by acidificying
h) Optionally alcohol
(b) dewatering/ filtration to provide filter cake
h) Optionally alcohol
(c) re-suspending
(d) adjusting pH
(e) dewatering/ filtration to provide filter cake
h) Optionally alcohol
(f) washing and dewatering
h) Optionally alcohol
(g) drying
Lignin

Fig. 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE2017/050663

A. CLASSIFICATION OF SUBJECT MATTER

IPC: see extra sheet

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: B01D, C08H, C08L, C09J, D01F, D21C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE, DK, FI, NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, PAJ, WPI data, BIOSIS, COMPENDEX, MEDLINE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 20160137680 A1 (THIES MARK C ET AL), 19 May 2016 (2016-05-19); abstract; paragraphs [0030]-[0031], [0034], [0036], [0051]; claims 10-11	1-11, 13-15
Y	--	12
A	SJÖSTRÖM, E. "Composition of Black Liquor" In: Wood Chemistry Fundamentals and Applications, San Diego: Academic Press, 1993, p. 158-161, ISBN 0-12-647481-8, see p. 159; whole document	1-15
	--	
Y	WO 2014116150 A (VALMET POWER AB ET AL), 31 July 2014 (2014-07-31); abstract; page 9, line 11 - line 17; claim 1	12
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☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
24-08-2017	30-08-2017

Name and mailing address of the ISA/SE	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE2017/050663

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 20160076199 A1 (LIQUID LIGNIN COMPANY LLC), 17 May 2016 (2016-05-17); whole document --	1-15
A	ÖHMAN, F., WALLMO, H., THELIANDER, H., "A novel method for washing lignin precipitated from kraft black liquor - Laboratory trials" In: Nordic Pulp and Paper Research Journal, 2007, Vol.22, No. 1, p. 9-16, ISSN 0283-2631; whole document --	1-15
A	US 20140186627 A1 (PU QIUSHENG ET AL), 3 July 2014 (2014-07-03); whole document --	1-15
A	WO 2012161865 A1 (LIQUID LIGNIN COMPANY LLC ET AL), 29 November 2012 (2012-11-29); whole document --	1-15
A	WO 2015185794 A1 (ANDRITZ OY), 10 December 2015 (2015-12-10) --	1-15
A	DE 102014108841 B3 (TECH UNIVERSITT HAMBURG HARBURG ET AL), 28 May 2015 (2015-05-28); whole document --	1-15
A	US 20080214796 A1 (TOMANI PER ET AL), 4 September 2008 (2008-09-04); whole document -- --------	1-15

International application No.
PCT/SE2017/050663

Continuation of: second sheet

International Patent Classification (IPC)

C08H 7/00 (2011.01)
B01D 11/00 (2006.01)
D21C 11/00 (2006.01)
C08L 97/00 (2006.01)
C09J 197/00 (2006.01)
D01F 9/17 (2006.01)

US	20160137680	A1	19/05/2016	NONE			
WO	2014116150	A	31/07/2014	CA	2898449	A1	31/07/2014
				EP	2948590	A1	02/12/2015
				US	20150322104	A1	12/11/2015
US	20160076199	A1	17/05/2016	NONE			
US	20140186627	A1	03/07/2014	NONE			
WO	2012161865	A1	29/11/2012	CA	2864689	A1	29/11/2013
				US	9187512	B2	17/11/2015
				US	20140200334	A1	17/07/2014
WO	2015185794	A1	10/12/2015	CA	2947971	A1	10/12/2015
				EP	3152359	A1	12/04/2017
				FI	126369	B	31/10/2016
				FI	20145519	A	07/12/2015
				US	20170159238	A1	08/06/2017
				UY	36127	A	30/11/2015
DE	102014108841	B3	28/05/2015	DE	112015002989	A5	06/04/2017
				WO	2015197048	A1	30/12/2015
US	20080214796	A1	04/09/2008	US	8172981	B2	08/05/2012