

ALIEN PROPERTY CUSTODIAN

MANUFACTURE OF CATION-EXCHANGERS

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The invention relates to the manufacture of cation-exchangers from lignin substances, specific details are following hereafter.

It is known to prepare exchangers for bases by treating wood, lignite and mineral coal at low temperatures with sulfonating agents such as concentrated sulfuric acid. If, however, this method is applied to difficultly soluble or insoluble lignin substances, the utilization of which is particularly desired with regard to the fact that large quantities thereof are available, feebly cation-active substances are obtained whose stability, however, especially when they are exposed to the action of alkaline agents, does not live up to the requirements which it has to fulfill.

Now, we have found that these drawbacks can be avoided by first condensing in an alkaline medium the lignin substances difficultly soluble or insoluble in water with water-soluble sulfites, for instance sodium sulfite or sodium bisulfite, and formaldehyde. A water-soluble sulfonic acid is thereby obtained which, after evaporation to dryness, is treated at temperatures up to about 100° C, preferably at about 80° C, with sulfonating agents such as concentrated sulfuric acid, fuming sulfuric acid, sulfuric acid anhydride, chlorosulfonic acid or the like. Thereby, a water-insoluble mass capable of exchanging cations is obtained which, in comparison with the product obtained directly from the lignin by means of sulfonating agents, is considerably more active and more stable to alkalis and also to mechanical strain. It may be of advantage in the after-treatment with the sulfonating agents to add further quantities of formaldehyde.

The process may be carried through with substances difficultly soluble or insoluble in water, which are obtained by treating with alkalis, preferably under pressure, lignin-sulfonic acids, particularly those obtainable from pine wood or hard

wood; it may further be carried through with lignins which are obtained by acidifying the so-called black liquors obtained in the soda wood-pulp process, for instance by means of carbonic acid. The so-called "nitro-lignin" obtained by decomposing wood by means of nitric acid is likewise applicable.

The following examples serve to illustrate the invention, but they are not intended to limit it thereto; the parts are by weight, unless otherwise stated:

Example 1.—200 parts of finely pulverized lignin-sulfonic acid, desulfonated to a considerable extent by means of alkalis, are introduced, at 80° C, while vigorously stirring, into a solution of 40 parts of caustic soda in 200 parts of water. Thereupon, 40 grams of solid sodium bisulfite are slowly added to the solution and finally 160 parts by volume of formalin of 32 per cent strength. The mass is then stirred for 6 to 8 hours at 80° C until the smell of formaldehyde is no longer noticeable, and after additions of 200 parts of water, rendered just acid to Congo paper by means of sulfuric acid. The solution is evaporated to dryness; part of the residue is stirred into about 3 to 4 parts by volume of concentrated sulfuric acid, and kept for about 4 hours at 80° C. After washing and drying the black granular product obtained is strongly cation-active.

Example 2.—According to Example 1, 200 parts of lignin-sulfonic acid desulfonated to a large extent by means of alkalis are introduced into a solution of 20 parts of caustic soda in 200 parts of water. 48.5 parts of sodium sulfite and 160 parts by volume of formalin of 32 per cent strength are then added. The condensation is complete after about 4 hours. It is then further worked up as described in Example 1.

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