

# ALIEN PROPERTY CUSTODIAN

## CONDENSATION PRODUCTS AND PROCESS FOR MAKING THEM

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This invention relates to products of condensation to be used as tannins and process of making said products.

I have found that technically valuable products of condensation may be obtained if sulfite waste liquor is condensed with aromatic sulfamides and aldehydes, especially formaldehyde or substances giving off formaldehyde. By this process the tanning properties of the sulfite waste liquor are improved to such an extent that the products of condensation will form valuable tannins, while the sulfite waste liquor itself, as known, can only be regarded as auxiliary tannin.

By the term "sulfite waste liquor" there should be understood the waste liquor obtained when disintegrating wood according to the sulfite process and the like, or the concentrates or dry substances that are obtained by evaporation and preferably freed from iron and lime.

Aromatic sulfamides or their nucleus substitution products which come into consideration as initial materials for the present process are for instance: benzene sulfamide, 4-toluol sulfamide, 4-chlorbenzene sulfamide, benzene-1,3-disulfamide, diphenyl-4,4'-disulfamide, naphthalene-1,3,5-trisulfamide, carbazol-tetrasulfamide, benzoic acid-3-sulfamide, 2-oxy-benzoic acid-5-sulfamide, benzoic acid-3,5,-disulfamide, phenol-2,4,6-trisulfamide, 1-oxy-naphthalene-8-sulfamide, 1-oxy-naphthalene-8-sulfamide-3-sulfo-acid and so forth. For the present process are furthermore suitable the sulfamides which are obtained by the action of ammonia onto the resinous sulfochlorides obtained by sulfonation, for instance, with chlorosulfonic acid, of cyclic compounds of the aromatic type, for instance, of benzene, naphthalene or their nucleus substitution products or of carbazol, pyridine, thiophene and the like in presence of tetrachloride of carbon. These resinous products comprise sulfochloride groups and are of viscous constituency in heated condition, while being of hard constituency and of brown color in cold condition.

The hydrocarbon radicals of the sulfamides may comprise quite generally substituents, such as methyl-, ethyl-, hydroxyl-groups, halogen and the like or also hetero-atoms and heteroatom-groups, such as for instance ether-, sulfone-, ester-, sulfonamide-, carbonamide-groups and so forth.

As aldehyde components for the present process mainly formaldehyde, acetaldehyde, glyoxyl, acrolein, croton-aldehyde, furfurol etc. or also corresponding compounds giving off aldehyde come into consideration, such as para-formaldehyde,

trioxy-methylene, formaldehyde-bisulfite, methylal, hexa-methylene-tetramine etc.

The process may also be conducted in such a manner that first preliminary condensation products are formed from the sulfamides and the aldehydes and that thereupon these products are caused to act onto the sulfite waste liquor. As known condensation products of this kind there may be mentioned the N-methylol compounds of the sulfamides and their halogen-hydracid esters, that are the N-halogen-methyl compounds of the sulfamides, which compounds may be obtained in known manner by action of the aldehydes onto the sulfamides, eventually by the use of proper amounts of hydrochloric-acid.

The conversion between the initial materials and the sulfite waste liquor takes place in an aqueous medium by heating to temperatures of about 100°. The conversation is completed as soon as the condensation product is soluble clear in water.

### Example 1

640 parts by weight of sulfite waste liquor freed from iron and lime and treated by evaporation as far as to powderous constituency with a dry content of 93.6% are stirred together with 360 parts by volume of water, until a homogeneous syrup is formed. Now 250 parts by weight of N-methylol-p-toluol sulfamide are added and the mixture, after having become homogeneous by stirring, is heated to 90° and stirred at this temperature, until a sample of this mass is soluble clear in much cold water. After dilution with water and adjustment of the suitable pH value the product is ready for use as a tannin.

### Example 2

426 parts by weight of a finely powdered technical mixture of benzene-1,3-disulfamide and benzene-1,4-disulfamide, such as is obtained by energetic sulfonation of benzene with excessive chlorosulfonic acid and conversion of the isolated mixture of benzene-1,3-disulfochloride and benzene-1,4-disulfochloride with ammonia are added to the syrupy sulfite waste liquid obtained according to Example 1 and the mixture well stirred. Thereupon 170 parts by weight of a solution of 40% aqueous formaldehyde are stirred into this mass at a temperature between 20 and 25° within a time amounting to two hours, stirring being continued at ordinary temperature for about 5 hours. Now the mass is heated to a temperature between 90 and 100° and this temperature maintained for about three hours, whereupon a sample of the mass shall be soluble clear in water.

If this is the case, the reaction mixture is evaporated to dryness at reduced pressure and at the temperature of the water bath. The residue which is obtained yields 888 parts by weight and may easily be ground, whereupon it will form a brownish gray powder which is readily soluble in water. The product is an excellent tanning agent.

In the aforegiven Example the benzene disulfamide may be replaced by 250-300 parts by weight of naphthalene-1,3,5-trisulfamide or naphthalene-1,3,6-trisulfamide or by the same amount of a technical mixture of isomeric naphthalene-trisulfamides. With the same mode of working a product is obtained which is similar to the afore described product.

### Example 3

The benzene disulfamide according to Example 2 is replaced by 266 parts by weight of a sulfamide having a nitrogen content of 10.5%, which sulfamide had been made by action of concentrated ammonia water from a resinous sulfochloride obtained from naphthalene. The mode of working is in other respects the same as according to Example 2. In this case also there will be obtained a powderous tannin which is easily soluble in water.

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