UNITED STATES PATENT OFFICE.

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PROCESS FOR HARDENING CONDENSATION PRODUCTS FROM PHENOLS AND ALDEHYDES.

965,823. Specification of Letters Patent. **Patented July 26, 1910.**

No Drawing. Application filed December 21, 1908. Serial No. 468,634.

To all whom it may concern:

Be it known that I, HANS LEBACH, chemist, a subject of the German Emperor, residing at Ludwigshafen-on-the-Rhine, Germany, have invented a certain new and useful Process for Hardening Condensation Products from Phenols and Aldehydes, of which the following is a specification.

In the manufacture of acid- and alkali-proof insoluble objects from the condensation products of phenols and aldehydes it has been found, that for the perfect hardening of the products heating for hours and even days is necessary, which is prejudicial to the technical utilization thereof. It is clear that in consequence hereof, it will be necessary to have for the manufacture of large quantities of objects, such as bars, plates and the like, a very large quantity of molds as well, as large drying chambers which render the process correspondingly complicated and expensive.

I have found that a reduction of the duration of heating to a small fraction of the time hitherto necessary and at the same time a considerably better utilization of the molds may be obtained in a simple manner by the addition of acids to the finished, condensed but still fluid mass.

The advantages of the process working without the addition of acids in comparison with that which employs acid from the beginning (*e. g.* German Patent No. 112685) consist mainly in the fact that the condensation can be interrupted at a point which appears suitable and the fluid or semi-solid product thus obtained (with or without filling substances) kept unchanged for months until further operated upon or sent away and further operated upon in another place, whereas the presence of the acid in the method of the German Patent No. 112685 does not permit any interruption, as the reaction would then proceed further of itself, until the solid final product was formed. In the present improvement the advantages of the two methods are combined by adding the acid at any convenient time after the condensation has been completed and at the instant when the polymerization to the hard, insoluble final product is to take place. The selection of the acids and the quantity thereof will depend upon the quantity and nature of the condensation product to be treated. It is advantageous to introduce the acids into the condensation products in a form, in which they combine with the latter more intimately, than is the case with acids diluted with water. This may be effected by diluting the acids with substances which are easily miscible with the products of condensation, such as ethyl-alcohol, glycerin and similar bodies. The products thus obtained are still more homogeneous than those obtained by means of aqueous acids.

Instead of adding free acids to the condensation products to accelerate their hardening, I may employ substances, which readily yield acids by decomposition, such as inorganic and organic acid chlorids, sulfuric acid esters, aluminium chlorid. Finally the reaction may be materially accelerated by means of acid salts, which are thus suitable for the present purpose. These additions may be used either as such, or dissolved in suitable solvents.

A special advantage of the new method is also that in the rapid solidification the vaporization of water still present and the formation of pores thereby is avoided, so that perfectly homogeneous masses are produced. It is also possible by this method and by using acid to let the solidification proceed at first only to a plastic intermediate stage, then after rapidly cooling down, to work it as may be desired and then further heat the parts operated upon. In like manner the action of the acid may take place in the interior of wood and other substances. In order to remove adhering traces of acid it is advisable to treat the hardened parts before or after further treatment undertaken in some cases, with vapors or solutions of alkalies or substances reacting in an alkaline manner, such as ammonia, soda solution, sodium acetate and if necessary under increased or reduced pressure.

In the specification of the German Patent No. 157553 is described a method in which a solid body is isolated by the addition of acid from a condensation mixture of phenol and aldehyde produced by the action of alkalies. This product however, in contradistinction to the one obtainable by the present method is soluble in various solvents, such as alcohol, acetone, alkali lyes and ammonia, and, when heated alone or in solution evolves formaldehyde; it differs therefore sharply from the completely insoluble heat-resisting products of the present method, the

formation of which in this way was not to be foreseen.

The present method differs from the one described in German Patent No. 112685 by the acid being not added until the condensation is completed, from which follow the other great technical advantages mentioned above.

The following examples will serve to further explain this process:—

Example I: 1000 parts of phenol, 1000 parts of 40% formaldehyde and 100 parts of crystallized sodium sulfite are heated until after being vigorously boiled up a light yellow viscous liquid is formed. To this is added after it has cooled 600 parts of wheat starch and 200 parts of 20% sulfuric acid and the whole is heated in suitable molds for from 1 to 2 hours at 85° C. After this time the mass has solidified to a hard, highly lustrous, insoluble product, which after being thoroughly washed with 10% soda solution, admits of being dyed, bored, ground and polished in a simple manner.

Example II: 1000 parts of phenol, 1000 parts of 40 per cent. formaldehyde and 100 parts of crystallized sodium sulfite are heated to boiling point for a quarter of an hour, 500 to 600 parts are distilled off, and the residual liquid is well mixed with 600 parts of wheat starch. Subsequently 150 parts of a mixture of 10 parts of sulfuric acid and 90 parts of glycerin are added in the cold, and the product is heated in suitable molds to 60° C. for about half an hour, whereby the whole is caused to solidify to a reddish solid mass of brilliant surface free from pores. This mass is then heated with gaseous ammonia in a closed receptacle for an hour, in order to neutralize the acid. It is advantageous to heat the mass subsequently to about 100° C., with the object of increasing its hardness and strength, but this is not absolutely necessary.

Example III: Instead of adding to 100 parts of the mixture a mixture of sulfuric acid and glycerin, as in Example II, 10 parts of a 25 per cent. aqueous solution of potassium bisulfite or 5 parts of benzoylchlorid are added, in which case also solid homogeneous masses with brilliant surfaces are obtained as before.

What I claim is:—

1. The process for accelerating the hardening of condensation products from phenols and aldehydes formed without the use of acids, which consists in adding acid to the products after the condensation, but before they have completely hardened, substantially as described.

2. The process for accelerating the hardening of condensation products from phenols and aldehydes formed without the use of acids, which consists in adding to the products after the condensation, but before the complete hardening of the same, an acid in the shape of a solution produced with a solvent other than water, substantially as described.

3. The process for accelerating the hardening of condensation products from phenols and aldehydes formed without the use of acids, which consists in adding to the product after the condensation, but before the complete hardening of the same, a substance, which readily yields acid, substantially as described.

4. The process for accelerating the hardening of condensation products from phenols and aldehydes formed without the use of acids, which consists in acting on the condensation products, before they have completely hardened, with an acid salt, substantially as described.

5. The process for producing a solid material from aldehyde and phenol, which consists in causing bodies of the phenol group to act on formaldehyde by applying heat until a uniform viscous mass is obtained, adding an accelerator to said mass, bringing said mass into the desired form, and maintaining said mass at a temperature below 100° C.

6. The process for producing a solid material from aldehyde and phenol, which consists in causing bodies of the phenol group to act on aldehyde by applying heat until a uniform viscous mass is obtained, adding an accelerator to said mass, bringing said mass into the desired form, and maintaining said mass at a temperature below 100° C.

In testimony whereof I have hereunto set my hand in presence of two subscribing witnesses.

HANS LEBACH.

Witnesses:

HANS SCHRAUBE,

H. TAEGER.