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METHOD FOR THE PRODUCTION OF PRESS MASSES

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This invention relates to a method for the production of press masses, and in particular of storage-proof quick or rapid press masses from urea and formaldehyde, and an acid dissociating hardening medium.

When producing press masses from urea-formaldehyde-resins, which masses have to satisfy all modern requirements such as quick press masses, it is necessary that, for the obtention of the very high water stability (boiling proof) and of the rapid hardening speed, besides the suitable condensation method and the correct urea-formaldehyde proportion, sufficient acid is at disposal in the press. Further, it is necessary that the mass for pressing shows at a temperature of 35 to 40° such storing stability that the flowing capability and the other pressing properties are not altered after storing for several months. A press mass corresponding to all requirements must further have the property that, during the pressing operation the acid comes to effect only gradually in order that during the flowing proceeding no hardening of the material takes place, as otherwise, especially when pressing large-size articles, dammings will occur which prevent the perfect pressing. The acid must, however, also not begin to act too late, as otherwise the hardening period is lengthened too much.

To satisfy all these requirements the acid in the press powder must be present in such form, that at temperatures from 35 to 40° no acid is split off, even after storing for months, and that the press powder shows an approximately neutral reaction. During the pressing operation the acid must be liberated only at a temperature which is near to 100°, in order that just sufficient time remains for the uniform outflow and that no damming occurs.

In patent specifications the ammonium salts of weak and strong acids, further the salts of hexamethylenetetramine, of organic bases such as aniline, methylamine, dimethylamine and trimethylamine or ethylamine, diethylamine, and triethylamine, ethanolamine and others are mentioned as substances giving off acid or developing acid. All these compounds have, however, the inconvenience that the salts either undergo strongly hydrolytic dissociation and therefore impart to the press powder a more or less strong acid reaction, or, as all urea-formaldehyde press masses contain small quantities of free formaldehyde or split off them during the storing, opportunity is given that by the formaldehyde the acid is gradually liberated during the storing, as is for instance the case with the ammonium salts. Other patents intend to obviate these inconvenlences by addition of acid anhydrides, such as anhydride of benzoic acid or anhydride of malonic acid and so forth, or esters of various kinds. All these compounds, however, become saponified in the course of time by the small quantities of water contained in any press powder and slowly cause acetification of the press masses. Other patents intend to solve the problem by employment of compounds such as for instance β-hydrobromic cinnamic acid or anhydrides of isodibromic succinic acid.

These compounds give off, however, acid only slowly during the pressing operation or they do not attain the necessary pH.

It has been found that a group of compounds shows all the above mentioned required properties, which group is produced if hexamethylenetetramine is treated with formaldehyde, i. e. 1 mol hexamethylenetetramine with at least 2 mol formaldehyde. In this manner a combination of these two compounds takes place, which is up to the present not yet explained and which represents a quite considerably stronger base than hexamethylenetetramine and the salts of which are only very weakly hydrolytically dissociated. One mol of this compound in n/1 normal solution with ½ mol HCl shows a pH of 6.2. A hexa solution of the same strength, to which ½ mol HCl is added, shows a pH of about 2.

The fatty acid salts of these novel hexamethylenetetramine-formaldehyde compound represent transparent gels, which are clearly soluble in aqueous urea-formaldehyde solutions. For hardening urea-formaldehyde resins gel-like mixed salts of fatty acids and of an other acid such as chloracetic acid, lactic acid or also mineral acid have proved as particularly suitable.

As the formaldehyde is apparently bound only loosely, these salts are always very resistant when care has been taken that no formaldehyde is consumed by any reactions. Only at temperatures near 100° the compound is rapidly dissociated and opportunity is thus given that the whole acid can fully act. Normal urea-formaldehyde condensates have always the tendency to split off small quantities of formaldehyde, and in these the said compounds are therefore very stable. By variation of the mol-proportion hexamethylenetetramine to formaldehyde it is possible, to alter the dissociation temperature of the compound. At about 1 mol hexamethylenetetramine for 3 mol formaldehyde the highest value is attained. Experiments to isolate the hexamethylenetetramine-formaldehyde compound (especially

fatty acid salts) allow to assume that 5 mol hexamethylenetetramine with 12 mol formaldehyde come together to form a monoacid base.

For special purpose the easily isolable, mostly well crystallising double salts of the hexamethylenetetramine-formaldehyde compound, from an acid and heavy metal salts or alkali salts or ammonium salts stood the test. Crystallised double compounds of hexamethylenetetramine-formaldehyde-acids and heavy metal salts have been described by Marcel Delepine C.r. de l'Académie des Sciences 127.622–25.

As suitable condensation methods of urea and formaldehyde or of urea-thio-urea and formaldehyde, all those methods have shown to be suitable, in which that smallest quantity of formaldehyde is employed, which results in a condensation product which does no longer take up further formaldehyde quantities.

Example 1.—One starts for instance from a product which is obtained if urea and formaldehyde in a mol-proportion of 1:1.3 to 1:1.5 at neutral reaction and temperatures of 30 to 40° are condensed during 48 hours. To the condensate which is obtained the gel-like compound of 12 g hexamethylenetetramine, 8 g lauric acid, 0.5 g chloracetic acid and 6 g formaldehyde are added to 360 g urea. Filling substances, such as for instance cellulose, are then worked into the mass which has been obtained, and the mixture is then treated in the usual manner, for instance shaped under heating by pressure. Instead of formaldehyde other aldehydes, aliphatic as well as aromatic, for instance benzaldehyde, can be brought together with hexamethylenetetramine and acids.

Example 2.—To a urea-formaldehyde condensation product which contains 360 g urea the gel-like mixture from 10 g hexamethylenetetramine and 6 g of palmitic acid, 2 g cetylic alcohol, 0.5 g maleic acid and 20 g cinnamic aldehyde are added as hardening medium, and the mixture thus obtained, which reacts approximately neutral, is kneaded with cellulose and treated in the usual manner to produce press powder. Instead of cinnamic aldehyde the equivalent quantity of benzaldehyde may be used.

The use of toluene-disulfamide resins has also proved to be advantageous, by which addition the flow and the water resisting property are further improved.

Instead of employing ready hexamethylenetetramine the working can be carried out so that by addition of ammonia to the condensate the hexamethylenetetramine is formed in the condensate itself. These compound types may be employed with great advantage also for the production of castings from urea-formaldehyde resins, as by keeping correctly increased drying temperatures it is possible to carry through the dehydration of the cast articles without hardening and to make the final acid hardening take place only at increased temperature.

Also hot varnishes of urea-formaldehyde resins give excellently brilliant elastic films when these compounds are used as hardening medium.

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