

# ALIEN PROPERTY CUSTODIAN

## HARDENING COLOPHONY

Reinard Ernst Vogel, Leutkirch (Allgau), Germany; vested in the Alien Property Custodian

No Drawing. Application filed July 9, 1941

The present invention relates to a method of hardening colophony.

Various methods have become known already to improve after a longer heating upon an elevated temperature the hardness and water stability of colophony by the addition of soluble phenolic or other products of condensation which by themselves and without colophony may form hard and soluble products. Moreover, the melting point of colophony has been elevated with an alteration of other characteristic properties by the fact that colophony in the presence of solvents has been treated with volatile halides particularly with HCl, Al Cl<sub>3</sub>, Ti Cl<sub>4</sub>, BF<sub>3</sub> (see *Chemisches Zentralblatt* 1933, Volume II, Page 3628, French Patent 734,390 and 1935 Volume II, Page 135, German Patent 609,754).

Now a new way has been found to increase the hardness and the water stability of colophony by formaldehyde in the presence of strong organic acids. If colophony is heated for a longer period of time with formaldehyde for substances separating formaldehyde, for instance with a marketable formaldehyde solution, and with a polybasic organic acid, then after all the water has been removed and the melt has obtained a temperature up to 200°-210° C, a considerable elevation of the melting point and of the water stability is obtained. Nothing prevents esterification of the colophony at a temperature of 250° C. Formaldehyde loosely embedded in or added to colophony does not come into consideration in this case, because the so treated product has no longer the smell of formaldehyde or discharges such smell. All two- or three-basic organic acids also the inorganic hydrochloric acid in a percentage of 1-8% calculated to the resin may be employed. If no additional acid is used, then larger amounts of formaldehyde and considerable longer periods of reaction are required to obtain the same effect.

*Example*

	Parts
Colophony .....	30
Formaldehyde, 30% by weight.....	60
Oxalic acid .....	2.5

are boiled for 6 hours under reflux condensation and then the temperature is slowly raised during 3-4 hours to 210° C. The melting point of colophony raised from 58°-69° C. to 103-109° C. The specific viscosity of a 40% solution spec/C in benzene amounted to 0.0306, whereas the same colophony with the same oxalic acid treated in the same manner but without the use of formaldehyde had a melting point of 63°-67° C. and a specific viscosity of spec./ C=0.0186, i. e. less than 39%.

According to the method disclosed in the German Patent 352,521 colophony is treated with furfural in the presence of acids. Furfural is a

heterocyclic aldehyde of the group of furfural and therefore behaves like an aldehyde and as an olefin oxide. In the heat furfural alone with acids forms resins (see American Patent 1,682,934) in contradistinction to formaldehyde. The German patent mentioned above, shows that in this case also no hardening of colophony occurs, but a resin formation of furfural is embedded, or, if in the most favorable case a hardening in the sense of a pure aldehyde would occur respectively the formation of furfural resin would inevitably result in parallel. Therefore, it cannot be concluded that formaldehyde may be employed instead of furfural. In all examples sulfur- or hydrochloric acid is used as catalyzer. The final product is a deep black resin (see page 1, line 17), whereas according to the method of the present invention no change of color of the colophony occurs.

In accordance with the method disclosed in the German Patent 203,847 operation is effected in such a manner that colophony is solved in alcohol and the formaldehyde is caused to act in the presence of a large amount of a strong acid in liquid form, for instance hydrochloric acid, formic acid or acetic acid. The hardening may occur at low temperature or at the boiling point of alcohol respectively (see page 1 lines 19-21). According to the method of the present invention, polybasic organic acids only are used by which the product is not dark colored as is the case in connection with hydrochloric acid, and which allow to effect the hardening in ordinary varnish boilers (formed of aluminium, nickel or stainless steels).

The method claimed in this case has, moreover, the great advantage that the process may be carried out without using solvents. From the begin it is not to be expected that without dissolving colophony in a solvent, i. e. in the melt, due to the presence of polybasic organic acids and anhydrous formaldehyde solutions only the hardness and viscosity of the resin is increased. Due to the mode of operation according to the present invention a separation of the finished resin from the solvent and the acid is rendered superfluous and the acid may either be used in this condition or be esterified at 250° C., for instance by means of glycerine.

The U. S. Patent 1,243,312 is concerned with the treatment of colophony with formaldehyde vapors without the use of catalyzers. The period of time for hardening is extremely long compared with the method carried out in the presence of organic polybasic acids besides the fact that special apparatus are required to produce the formaldehyde gas and to lead the latter into the liquid resin.

REINARD ERNST VOGEL.