DETERMINATION OF PORE SIZE DISTRIBUTION BY SETARAM DSC-101 (THERMOPOROMETRY)

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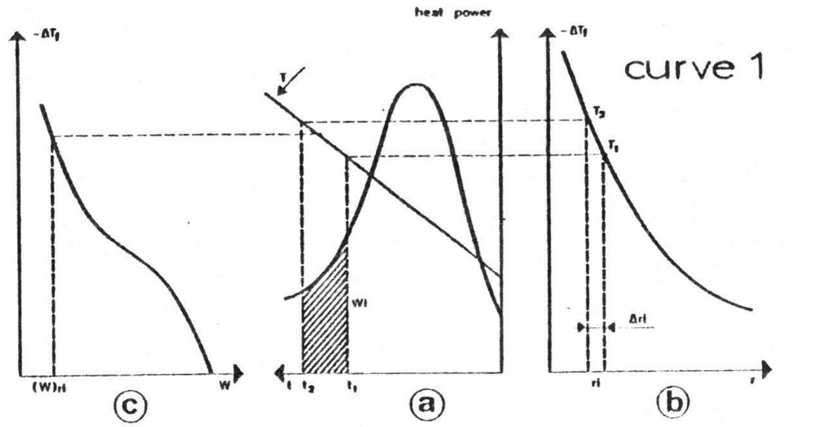
The use of porous matarials needs the knowledge of their structure and their pore size distribution.
The used technics (mercury porosimetry, B.J.H.) allow to determine this distribution but apply neither to compressible materials nor to materials swelling in their medium of use.
The calorimetric method, called THERMOPOROMETRY, uses the melting or solidification thermogram of a pure liquid contained inside the porous substance. (1-2-3).

PRINCIPLE.
The porous sample to analyze ist saturated with liquid and the solidification thermogram is observed.



transformation energy per volume unit of liquid = f (solidification temperature)

solidification thermogram

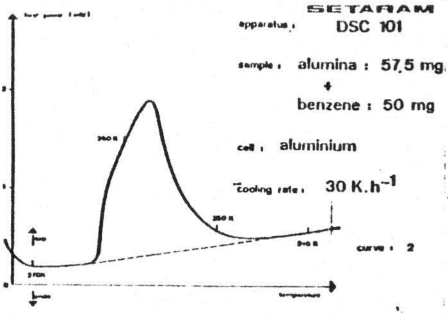
solidification temperature depression = f (pore radius)

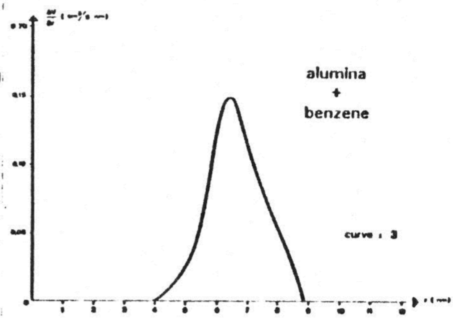
The curve a represents the thermogram. Between the instants t_1 and t_2 (the temperature varies from T_1 to T_2), a fraction of liquid has solidified evolving the energy W_i represented by the "dashed" area.
The calibration curve b giving the solidification temperature depression versus the pore radius allows to determine the correspondant pore size. - The calibration curve c gives the transformation energy per volume unit of fluid w versus the solidification temperature.

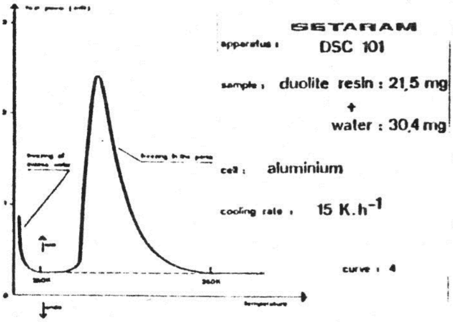
You can get the total volume ΔV_i of pores in the considered Δr_i radii range thanks to the values of W_i and correspondant w.
For various condensates, calibration curves can be estabisihed by means of the thermodynamic relation ships which link triple joint depression and transformation energy to the curvature of condensate particle.

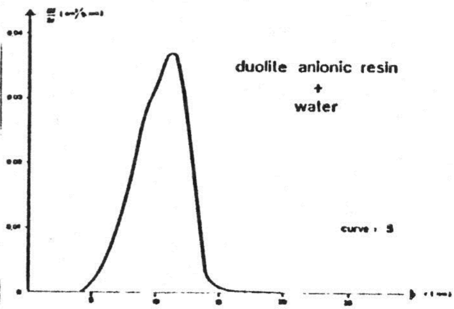
EXPERIMENTS.

The used calorimeter is the SETARAM DSC-101 with its subambient cooling system. - The samples are analyzed in aluminum cell. - The studied material is alumina saturated with benzene. - Before the record of the thermogram, the sample is first cooled down to about 250 K in order to produce cristallation germs, then heated up just below the normal freezing point. In that way the excess benzene stays frozen. - The curve recorded the cooling (curve 2) at $30 K \cdot h^{-1}$ shows only one exotherm due to solidification of benzene in the alumina pores.









The same test has also been carried out with water condensed in a duolite anionic resin (curve 4). - The pore size distributions are shown on the curve 3 and 5.

CONCLUSION.

The use of the SETARAM DSC-101 allows the study of pore-size distribution by the thermogrametry-method. This method has an application range of 20 to 2.000 Å. It measures the actual size of the pore cavity and not the pore opening as the traditional methods. Besides, the degree of hysteresis between the solidification and fusion thermograms give information on the pore shape.