A new procedure for solving the integral equation which connects the crystallite-diameter distribution function $p_v(D)$ to the pure diffraction profile is presented here. The representation of $p_v(D)$ is based on a polynomial expansion modulated by a generalized Cauchy function. The influence of the truncation of the diffraction profile and of the number of coefficients of the polynomial expansion is studied. This procedure has been applied with success to some catalysts, the granulometry of which is known by other experimental approaches.

**Introduction**

We have recently proposed a new deconvolution procedure (Moraweck, de Montgolfier & Renouprez, 1974, 1977) of X-ray diffraction profiles based on the search for the solution by an optimization method. This solution is represented by a polynomial damped by a function which minimizes the oscillations of the polynomial.

The pure diffraction profile, corrected for instrumental resolution, contains all physical information available from diffraction experiments. Crystallite size, strains and defects are normally obtained from the analysis of the successive orders of a given reflection. However, in the case of powders, the size effect turns out to be the major contribution to broadening and hinders an accurate measurement of high-order reflections. Moreover, from experiments performed by other techniques, it appears to be reasonable to consider that most of the measured broadening on fine metal or oxide powders is produced by size effects. (Moraweck, 1972; Fouilloux, Martin, Renouprez, Moraweck, Imelik & Prettre, 1972).

The aim of this paper is to show how a pure diffraction profile obtained in such a way can be used to determine a crystallite-diameter distribution function consistent with the results obtained by other physical methods, and to improve the texture determination of a finely divided solid.

We know that the crystallite-diameter distribution function can be obtained from the Fourier transform of the pure diffraction profile with the equations given by Bertaut (1950) and Warren & Averbach (1950). Such a method is very sensitive, as shown by Young, Gjerdes & Wilson (1967), to spurious oscillations of the transform, which lead to anomalous oscillations of the distribution curves. Such oscillations are not related to the texture of the solid since their negative parts have no physical meaning.

More recently, improvements of the method based on the Stokes (1948) method have been proposed by Moraweck (1972), de Bergevin & Germi (1972), Păușescu, Mănăilă, Popescu & Jijovici (1974). The aim of these methods was to suppress parasitic oscillations: they were based on the use of an asymptotic law to describe the tails of the diffraction profiles. However, this analytical form is subject to controversy.

Bertaut (1950) showed that the relation between the crystallite-diameter distribution function, $p_v(D)$, and the pure diffraction profile, $I(s)$, is:

$$I(s) = K \int_0^\infty D \frac{\sin^2(\pi Ds)}{(\pi s)^2} p_v(D) dD.$$  \hspace{1cm} (1)

Defining the mean volume diameter, $D_v$, as (Moraweck & Renouprez, 1968):

$$D_v = \int_0^\infty D p_v(D) dD$$

and remembering that $p_v(D)$ is the volume fraction of the sample, the diameter of which is in the range $(D, D + dD)$, (Bertaut, 1950)

$$I(0) = K \int_0^\infty D p_v(D) dD = K D_v.$$  \hspace{1cm} (2)

Combining (1) and (2) leads to:

$$f(s) = \frac{I(s)}{I(0)} = \frac{1}{D_v} \int_0^\infty D \frac{\sin^2(\pi Ds)}{(\pi Ds)^2} p_v(D) dD.$$  \hspace{1cm} (3)

The last equation is a different formulation of the relation obtained by Hossfeld & Oel (1966), who
numerically solved (3) by the Gauss-Seidel iterative method.

**Method**

The unknown function \( p_s(D) \) can be computed from (3), if the function \( f(s) \) is given step by step. This type of problem has been treated by one of us in a similar case (de Montgolfier, Martin & Dalmon, 1973): the problem was to determine the magnetic-domain distribution function from the integral equation relating the magnetization of the ferromagnetic domains to the intensity of the magnetic field. This equation involves a kernel which is the Langevin function and has been solved by approaching \( p_s(D) \) by a polynomial expansion damped by a Gaussian function in order to ensure a rapid convergence of the representation. Here, the Langevin function is replaced by the diffraction kernel:

\[
D \sin^2 \left( \frac{\pi Ds}{D_c} \right) (\pi Ds)^{-2}.
\]

Taking advantage of our previous experience, we approximate the crystallite-diameter distribution function \( p_v(D) \) to:

\[
p_v(D) = \left[ 1 + \alpha^2 (D - \gamma)^2 \right]^{-\beta} \sum_{i=1}^{\infty} a_i D_i = A(D) q(D).
\]

The generalized Cauchy function is aimed to ensure the decreasing of \( p_v(D) \) to zero as \( D \) goes to infinity.

The integral equation (3) becomes:

\[
\phi(s) = \int_0^{D_m} k(s, D) A(D) q(D) dD
\]

where

\[
k(s, D) = \frac{D}{D_c} \cdot \frac{\sin^2 \left( \frac{\pi Ds}{D_c} \right)}{(\pi Ds)^2}.
\]

\( f(s) \) is given step by step \((m \text{ points } j)\), and:

\[
\varphi_j = \int_0^{D_m} k(j, D) A(D) q(D) dD.
\]

(4)

\( D_m \) is the upper limit of integration which may be chosen at about three or four times the value of \( D_c \).

Now, we introduce the generalized moments \( \mathcal{M}_i \) of \( p_v(D) \) such that:

\[
\mathcal{M}_i(j) = \int_0^{D_m} k(j, D) A(D) (D - \gamma)^i dD
\]

and (4) becomes:

\[
\varphi_j = \sum_{i=1}^{n} a_i \cdot \mathcal{M}_i(j).
\]

Moreover, the calculated function \( \phi(s) \) must be as close as possible to the function \( f(s) \). In order to compare the given values of \( f(s) \), \( f_j \), and the calculated values of \( \phi(s) \), \( \phi_j \), we require that the sum of the squares of the differences between \( \phi_j \) and \( f_j \) must be a minimum, therefore:

\[
S = \sum_{j} (f_j - \phi_j)^2 f_j^{-2} \text{ minimum}.
\]

We thus obtain a set of simultaneous equations which are nonlinear functions of parameters \( \alpha, \beta, \gamma \). A classical method of matrix inversion is not directly available. We must, therefore, use another method for obtaining the correct values of the parameters. We minimize \( S \) by using the so-called 'flexible simplex' method, which gives, for each step of optimization, a set of \( \alpha, \beta, \gamma \) values for which the \( S \) function decreases. The process is stopped when a sufficient precision for \( S \) is reached.

**Tests of the method**

The program and the method have been checked by applying them to an 'ideal' diffraction profile (see Fig. 1) built up from an experimental distribution function obtained elsewhere by Moraweck (1972). Numerical integration of (3), where \( p_v(D) \) is the previous function,
leads to a function \( f(s) \) tabulated for \( s \) varying from \(-0.06 \) to \(+0.06 \) \( \text{Å}^{-1} \), the ratio of minimum to maximum height of \( f(s) \) being \( 0.005 \). The procedure defined here was then applied to this function, setting the number of polynomial coefficients to 5 and the definition range of \( D \) to \( 0-152 \) \( \text{Å} \). Under these conditions the program yields a distribution function to be compared with the exact function: the relative difference between these two functions is lower than \( 10^{-3} \) for each point (see Fig. 2) and the calculated mean volume diameter is equal to the true one, \( \text{i.e.} \ 62 \text{Å} \).

### Influence of the degree of the polynomial

From Fig. 2, it is seen that the distribution curve \( p_\alpha(D) \) has two maxima, the abscissae of which are 45 and 128 \( \text{Å} \). Such a curve must be described by a polynomial of degree greater than \( n = 3 \): its first derivative must have at least three real roots.

It is of great interest to investigate whether the degree of the polynomial influences the general shape of the curve and its main features, as for example the abscissa of the maxima. Such a study was made starting from a degree \( n = 3 \). The results are summarized in Tables 1 and 2.

The values of the parameters, the polynomial coefficients and the distribution curve for \( n = 3 \) (Fig. 3) are quite different from the results for \( n \geq 5 \). It is impossible to fit such a distribution function by a third-degree polynomial damped by the function \( \left[ 1 + \alpha^2(D - \gamma)^2 \right] \). Moreover, Fig. 3 shows that a fourth-degree polynomial is unable to give a good agreement between the true and the computed distribution, although, in theory, the first derivative of such a polynomial may have three real roots. In this case, the damping function is too efficient (see Table 2). Furthermore, the experiment shows that, for obtaining a given precision, the computing time is at least six times larger for \( n = 4 \) than for \( n = 5 \). This solution is, therefore, unacceptable.

The question then arises whether a degree greater than \( n = 5 \) can be used to approach exactly the initial distribution. Although the values of the damping function parameters as well as the polynomial coefficients appear to be different (for \( n \geq 7 \)) no perceptible difference can be detected between the whole set of distribution functions for \( 5 \leq n \leq 9 \). For an appropriate value of the polynomial degree, \( n \), our process is thus able to yield the exact result for a given \( f(s) \) profile.

Consequently, in order to obtain the best representation of the distribution function, several trials have to be done in which the polynomial degree is increased by 2 at each step: when two consecutive trials give approximately the same result, we consider that the computed distribution function exhibits the main characteristics of the investigated sample.

#### Influence of profile truncation

It is well known that, in the Fourier method, truncation of the diffraction profile leads to meaningless oscillations.

### Table 1. Variations of \( \alpha, \beta, \gamma \) parameters versus the degree, \( n \), of the polynomial

<table>
<thead>
<tr>
<th>( n )</th>
<th>( \alpha \times 10^{-6} )</th>
<th>( \beta \times 10^{-7} )</th>
<th>( \gamma \times 10^{-9} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>13.79</td>
<td>6.7186</td>
<td>6.5986</td>
</tr>
<tr>
<td>4</td>
<td>6.357</td>
<td>6.0389</td>
<td>6.6822</td>
</tr>
<tr>
<td>5</td>
<td>3.124</td>
<td>1.274</td>
<td>1.503</td>
</tr>
<tr>
<td>6</td>
<td>5.7284</td>
<td>2.6236</td>
<td>4.5691</td>
</tr>
<tr>
<td>7</td>
<td>1.5107</td>
<td>2.6737</td>
<td>-0.8564</td>
</tr>
<tr>
<td>8</td>
<td>6.2003</td>
<td>7.7538</td>
<td>149.6445</td>
</tr>
<tr>
<td>9</td>
<td>149.6445</td>
<td>63.6924</td>
<td>1.0760</td>
</tr>
</tbody>
</table>

### Table 2. Variations of the polynomial coefficients versus the degree, \( n \), of the polynomial

<table>
<thead>
<tr>
<th>( n )</th>
<th>( x \times 10^{-3} )</th>
<th>( \beta \times 10^{-6} )</th>
<th>( \gamma \times 10^{-8} )</th>
<th>Computed precision ( \times 10^{-7} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>4002</td>
<td>2.6110</td>
<td>48.01</td>
<td>719.38</td>
</tr>
<tr>
<td>4</td>
<td>7383</td>
<td>93.1061</td>
<td>33.98</td>
<td>777.6</td>
</tr>
<tr>
<td>5</td>
<td>12078</td>
<td>1.0137</td>
<td>44.92</td>
<td>44.26</td>
</tr>
<tr>
<td>6</td>
<td>12789</td>
<td>1.3914</td>
<td>44.62</td>
<td>4.45</td>
</tr>
<tr>
<td>7</td>
<td>15759</td>
<td>0.6092</td>
<td>44.44</td>
<td>9.04</td>
</tr>
<tr>
<td>8</td>
<td>15751</td>
<td>0.6793</td>
<td>43.21</td>
<td>8.83</td>
</tr>
<tr>
<td>9</td>
<td>14830</td>
<td>1.0194</td>
<td>49.71</td>
<td>6.45</td>
</tr>
</tbody>
</table>
tions of the crystallite-diameter distribution function (Young, Gjerdes & Wilson, 1967).

We will experimentally show that our method is not very sensitive to truncation of the diffraction profile. For this purpose, the diffraction profile was truncated at successive values, so that the profile height fell to 6-7, 8-5, 11-4 and 16 % of its maximum value (see Fig. 1). Results are summarized in Tables 3 and 4.

Table 3. Variations of parameters \( x, \beta, \gamma \) versus the profile truncation

<table>
<thead>
<tr>
<th>Truncation (%o)</th>
<th>( x ) ( \times 10^{-2} )</th>
<th>( \beta )</th>
<th>( \gamma ) precision ( \times 10^{-6} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1-3078</td>
<td>1-1367</td>
<td>44-92</td>
</tr>
<tr>
<td>6-7</td>
<td>1-3660</td>
<td>1-2028</td>
<td>48-69</td>
</tr>
<tr>
<td>8-5</td>
<td>1-5068</td>
<td>1-1037</td>
<td>51-33</td>
</tr>
<tr>
<td>11-4</td>
<td>1-4454</td>
<td>1-7021</td>
<td>70-29</td>
</tr>
<tr>
<td>16-0</td>
<td>1-3315</td>
<td>1-2144</td>
<td>45-12</td>
</tr>
</tbody>
</table>

Table 4. Variations of the polynomial coefficients, \( a_i \) versus the profile truncation (for \( n = 5 \))

<table>
<thead>
<tr>
<th>Truncation (%o)</th>
<th>( a_1 ) ( \times 10^{-6} )</th>
<th>( a_2 ) ( \times 10^{-7} )</th>
<th>( a_3 ) ( \times 10^{-9} )</th>
<th>( a_4 ) ( \times 10^{-11} )</th>
<th>( a_5 ) ( \times 10^{-13} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>6-5986</td>
<td>7-8564</td>
<td>8-9848</td>
<td>22-1183</td>
<td>6-8241</td>
</tr>
<tr>
<td>6-7</td>
<td>1-3214</td>
<td>0-7527</td>
<td>0-2584</td>
<td>-4-8244</td>
<td>1-2144</td>
</tr>
<tr>
<td>8-5</td>
<td>-5-9269</td>
<td>-5-0435</td>
<td>-4-2886</td>
<td>2-7932</td>
<td>-5-7446</td>
</tr>
<tr>
<td>11-4</td>
<td>5-7284</td>
<td>5-1509</td>
<td>4-6627</td>
<td>0-3699</td>
<td>5-6036</td>
</tr>
<tr>
<td>16-0</td>
<td>-1-6950</td>
<td>-1-5571</td>
<td>-1-4429</td>
<td>-0-4785</td>
<td>-1-6633</td>
</tr>
</tbody>
</table>

We see that the variations of the \( x, \beta, \gamma \) parameters are relatively small and, although the \( a_i \) coefficients are quite different, the \( p_x (D) \) curves are practically identical, and only a 16 % truncation leads to some appreciable deviations: in our procedure, the numerical integration is performed, not on the experimental function \( f(s) \), as in the Fourier method, but on the modellized function \( p_x (D) \) which can be defined from zero to infinity.

Preliminary results

Two 220 experimental diffraction profiles have been obtained from samples of platinum (10 % weight) supported on alumina (sample I) and on calcinated alumina (sample II). Both corresponding pure diffraction profiles have been computed by the procedure described in the preceding part I. For obtaining their crystallite distribution function, we choose in both cases a polynomial of degree equal to 5; the computed distributions are shown on Fig. 4. The curves have negative parts, which are physically insignificant, and these solutions are therefore unacceptable.

However, let us compare the different kinds of mean volume diameters summarized in Table 5. From the integral breadth of the experimental and instrumental profiles and from the correction formula of Anantharaman & Christian (1956), we can compute a mean diameter \( \bar{D}_{AC} \); \( \bar{D} \) is obtained from the integral breadth of the pure diffraction profile, and \( \bar{D}_c \), from \( p_x (D) \) by equation (3). For the two samples the computed values are close. Therefore, although the \( p_x (D) \) solutions are physically incorrect, the mean volume diameters are coherent.

Improvements of the method

In some cases, as shown by experiment, the method previously described fails. If we consider the dotted curve on Fig. 5, we can see that, for a \( D \) value greater than 170 Å, this curve becomes negative. Although it is outside the chosen range, this negative part has no physical meaning. We saw, however, that such a polynomial approximation gave, in the selected range, a good representation of the physical phenomenon.

Such a negative part may come from two different origins. For example, the true minimum of \( S \) corresponds to a polynomial which exhibits negative ordinates in the chosen range of \( D \). Alternatively, the minimized quantity, \( S \), is a function of several parameters and represents a hypersurface with several minima. From an initial set of parameters, the numerical process ends up in a secondary minimum higher than

\[ p_x (D) \times 10^2 (\%o) \]

Fig. 4. Crystallite-diameter distributions for (1) sample I and (2) sample II (simple polynomial).

| Table 5. Comparison between different measurements of the mean volume diameter for two samples of Pt/Al_2O_3 |
|---------------------------------|--------|--------|--------|
|                                  | \( \bar{D}_{AC} \) | \( \bar{D} \) | \( D_c \) |
| Sample I                        | 61     | 62     | 58     |
| Sample II                       | 76     | 75     | 73     |
the absolute minimum. In both cases, physically meaningless solutions are obtained.

Let us suppose that the distribution curve presents a negative part at the origin. This can be eliminated by an optimization of the lower limit of integration, called $D_0$, and this value is taken as the origin of the polynomial [see equation (4)].

Therefore, (3) becomes:

$$f(s) = \int_{D_0}^{D_{m}} \frac{D \sin^2 (\pi D s)}{(\pi D s)^2} p_c(D) dD$$
and

$$p_c(D) = A(D) \sum_{i=1}^{n} a_i (D - D_0)^i.$$  \hspace{1cm} (5)

The experiment, however, shows that a negative part can appear in the intermediate range of $D$. The polynomial must, therefore, remain positive for any value of $D$. This can be made so by replacing the polynomial by its square value, i.e.:

$$p_c(D) = A(D) \left[ \sum_{i=1}^{n} a_i (D - D_0)^i \right]^2 = A(D) \varphi(D).$$

When this constraint is used, a new process is needed to solve the integral (1). (4) becomes:

$$\varphi_j = \sum_{i=1}^{n} a_i \mathcal{M}_i + k \alpha, \beta, \gamma, D_0.$$

The resulting system of simultaneous equations is no longer linear in the polynomial coefficients $a_i$. To solve (4), we must optimize the coefficients $a_i$ for each set of parameters $\alpha, \beta, \gamma, D_0$. The method is again the flexible simplex method.

**Experimental results and discussion**

In order to illustrate the method described in the last section, we chose two samples of platinum supported by $\gamma$-alumina (sample I) and $\gamma$-alumina calcinated at 600°C (sample II). After impregnation by a hexachloroplutinic acid solution, the samples are dried in air, then reduced at 400°C under a hydrogen flow for 16 h (Dartigues, 1975). The diffraction profiles are registered step by step with a Siemens diffractometer, with monochromatic $K\alpha_1$ radiation obtained from a Cu X-ray tube equipped with a quartz front monochromator. ($K\alpha_2$ radiation intensity is less than 1%). Moreover, the instrumental broadening obtained from an $\alpha$-alumina powder is found to be equal to 0·1° ($\theta_0$).

In order to get a solution similar to that obtained with a simple polynomial, we have to use the same number of independent coefficients. We shall use, therefore, nine coefficients for the squared polynomial.

The results concerning both samples of platinum supported on alumina are shown on Fig. 5 (curve 1, sample I) and Fig. 6 (sample II). On Fig. 5, we report, besides, the particle volume distribution curve as computed from X-ray small-angle scattering experiments (curve 2). The comparison of these two curves shows that the platinum particles supported on alumina are for the greater part polycrystalline: the abscissae of the distribution maxima are quite different.

In the case of sample II, we report on Fig. 7 the distribution curves obtained (1) from X-ray small-angle scattering and (2) by electron microscopy. (In the case of sample I, the latter method could not be used.)

To compute the distribution function shown by curve (2) on Fig. 7 we assume that the particles observed on the electron micrograph have a regular shape, mainly spherical. The same hypothesis was made for the particle-volume distribution function from X-ray small-angle scattering experiments (Donati, Pascal & Renouprez, 1967). A good agreement between the two curves is now obtained, especially in the diameter range extending from 10 to 40 Å.
By X-ray line-profile analysis, we obtain the same main characteristics of the crystallite-diameter distribution, the maximum of which is located at 25 Å. This means that the smallest particles detected by electron microscopy and X-ray small-angle scattering in the 10 to 40 Å diameter range are monocrystalline. Sample II contains a small number of particles larger than 40 Å most of which are polycrystalline, as shown by the lack of agreement between the three experiments (see Figs. 6 and 7).

It is well known that the sorption properties of a catalyst, and consequently its activity and selectivity, are strongly influenced by the structure of the solid, as shown elsewhere by Dartigues (1975) and Gault (1975) in the case of hexane isomerization. As it is admitted that unusual properties, such as variations in the symmetry of crystalline materials, appear in the smallest particles, it is important to determine precisely the diameter distribution functions to establish a correlation between the catalytic properties and the textural parameters.

References